

Some X-ray experiments on the orientation properties of synthetic rubber of polychloroprene type

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With 8 figures in the text

The purpose of this investigation was to make with polychloroprene some X-ray experiments of the same type as those which have been performed on the orientation and crystallinity of stretched natural rubber and to find, if possible, some method which could be used to characterize a given material. The orientation and crystallinity properties of natural rubber have been investigated by different methods (X-ray [1, 2, 3, 4], dilatometric [5], birefringence [6]); the crystallinity of neoprene has been investigated by dilatometric [7, 8] and infrared [9] methods but it seems that there are only few X-ray experiments concerning the crystallinity in the specimens.

Polychloroprene after stretching gives an X-ray diagram of the familiar fibre type (reported by many authors); unstretched it only gives a diffuse halo. With natural rubber one gets diagrams of the same general type, although, as Fig. 1 shows, the two diagrams of the elongated materials are quite different. In the investigations of the orientation in rubber with X-rays, use has been made of the fact that the halo and the spots may be measured separately; in the case of neoprene a somewhat different method was employed.

1. Some remarks concerning the intensity distribution in an interference circle from a fibre-oriented material

Consider a small crystalline powder specimen; the position of any plane in it can in the usual way be given by the coordinates of one of the two points where the normal to the plane intersects a reference sphere, placed with its center in the specimen and with a unit radius which is large in comparison with the dimensions of the specimen (Fig. 2). Each crystallite in the specimen contains different sets of parallel crystallographic planes having a common normal, which intersects the reference sphere in two diametrical points. The intensity in a small element of an interference ring depends, among other things, upon the amount of material scattering radiation to that element. In the following the amount of material scattering to an element of a given interference circle will be taken as a function of the orientation of a specimen of fibre type. In this paper the orientation is discussed in terms of the distribution of the positions of "a plane", by which is meant the distribution on the reference sphere of the normal intersections (points), corresponding to that special plane, from all the crystallites in the specimen. For a randomly spaced material the points

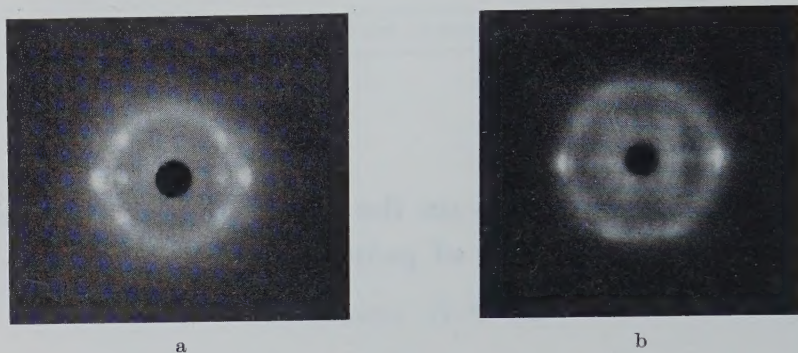


Fig. 1. (a) Natural rubber elongated 500 %. (b) Neoprene elongated 1200 %.

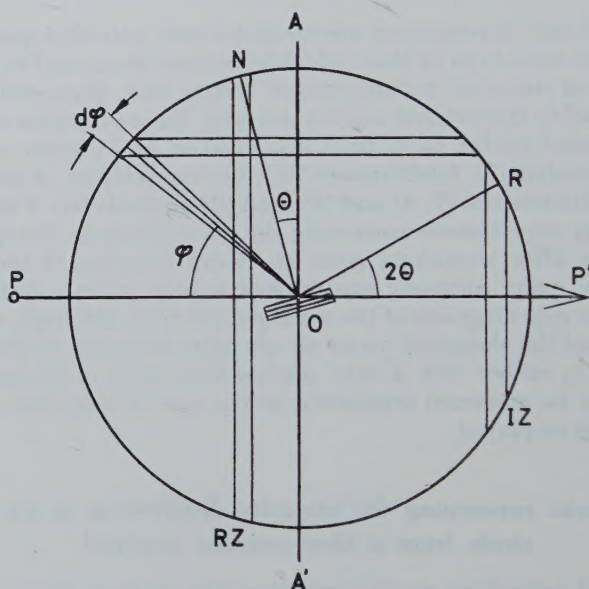


Fig. 2. Projection of the reference sphere on a plane containing the primary beam PP' and the fibre axis AA' . At O is a set of planes normal to the projection plane and with the normal ON and the reflected beam OR . RZ and IZ are the projections of the zone of reflection respective the zone containing the scattered radiation. Also the angles φ and θ are marked in the figure.

corresponding to a certain crystallographic plane will be evenly distributed over the surface of the sphere. If the specimen is oriented the distribution of the points (normal intersections) will no longer be random (compare [12]).

Obviously the distribution of the positions of a number of crystallites generally cannot be defined by the distribution of the positions of only one of the crystallographic planes. It seems, however, that for fibre materials the distribution of a plane, tending to parallelity with the fibre axis, in many cases gives a fairly good approximation of the crystallite distribution, even if the difference must always be

kept in mind. In any case the planes parallel to the fibre axis are the most easily accessible and most readily offer themselves to an investigation of this kind.

Consider a simple fibre orientation and define the intersection of the fibre axis with the sphere as the poles of the sphere. As a fibre orientation has rotational symmetry around the axis it is possible to describe the orientation of a given plane by a frequency function, $N(\varphi)$, which is defined in such a way that $n_0 N(\varphi) d\varphi$ gives the number of points in a narrow zone parallel to the equator. The angular distance from the equator to the zone is φ , the width of the zone $d\varphi$ and the total number of points on the reference sphere corresponding to the plane is n_0 . From these notations it follows that

$$\int_{-\frac{\pi}{2}}^{+\frac{\pi}{2}} N(\varphi) d\varphi = 1. \quad (1)$$

If absorption and extinction are neglected, the total amount of radiation diffracted from a plane in a powder specimen of small mosaic crystals is given by the well-known equation [11]

$$P = \frac{1}{2} I_0 p Q V \cos \theta \quad (2)$$

where

P = the total amount of radiation per second in the whole cone of diffraction

I_0 = the amount of incident radiation per second and square centimeter

p = the planar factor

θ = the glancing angle

V = volume of specimen in the primary beam

and

$$Q = \left\{ \left(\frac{Ne^2 F(hkl)}{m c^2} \right)^2 \lambda^3 \frac{1}{\sin 2\theta} \frac{1 + \cos^2 2\theta}{2} \right\} \quad (3)$$

The notation in equation (3) is

N = the number of primary cells per cm^3

e = the electron charge

m = the electron mass

c = velocity of light

$F(hkl)$ = the structure factor

λ = the wavelength of the radiation.

Bragg's equation

$$n\lambda = 2d \sin \theta \quad (4)$$

gives a connection between the spacing, d , of a set of planes, the wavelength and the glancing angle of the diffracted radiation. The order of reflection is denoted by n . In this paper, however, the orders higher than the first are neglected.

If the diffracted radiation is registered in a plane normal to the primary beam (e.g. on a photographic plate), the intersection between the plane of the film and the cone of diffracted beams gives the interference circle. The intensity of the scattered radiation is defined as the amount of radiation scattered per unit of arc of the circle and denoted by I . Thus we have

$$I = \frac{P}{2\pi} = I_0 Q p \frac{\cos \theta}{4\pi} V. \quad (5)$$

The well-known condition for a plane to give a reflection is that its normal intersects the reference sphere within a narrow zone called the zone of reflection which is defined by the glancing angle θ and is concentric with the primary beam. The angular distance of the zone from the point where the primary beam enters the sphere is $(\pi/2 - \theta)$. As a randomly spaced specimen has the points evenly distributed over the sphere, the density of points is the same in the different parts of the zone of reflection and the intensity of the diffracted radiation is the same all over the interference circle. For an oriented specimen, as for a disordered one, the intensity in a small sector of the interference circle is proportional to the part of the irradiated material which lies in position for reflection to that sector. The density of points in any part of the zone of reflection can easily be calculated for a fibre specimen if the previously mentioned function $N(\varphi)$ is known, and assuming average crystallites the intensity in the corresponding sector of the interference circle can be determined. Conversely, for those zones of the reference sphere which are covered by the reflection zone, the values of $N(\varphi)$ can be determined for a plane if the distribution of intensity in the corresponding interference circle is measured. Obviously the intensity in an interference circle depends only upon the density of points on those parts of the sphere for which $\varphi \leq (\pi/2 - \theta)$.

It is easily shown (see appendix A) that the intensity of a reflection from a plane in a fibre oriented specimen is

$$I_\alpha = \frac{I_0 p Q \cos \theta \cdot V \cdot N(\varphi)}{2\pi \cos \varphi} \quad (6)$$

where I_α is the intensity on the interference circle at an angle α measured along the circle from the equator of the diagram; α corresponds to the angle φ on the reference sphere. The other notations are the same as before. It may be assumed that the primary beam is normal to the fibre axis and in this case the connection between the angles α , φ and θ is given by the relation [14]

$$\sin \alpha = \frac{\sin \varphi}{\cos \theta}. \quad (7)$$

In derivation of equation (2) it is assumed that the zone of reflection is narrow. With crystalline high polymers this condition may not be fulfilled which could give an error in the intensity values. However, an estimation gave the result that this error is not large enough to be of importance in the present case.

Values, which can be used to characterize a given specimen, may be obtained from an interference due to a plane tending to parallelity with the fibre axis. In the following, the discussion is mainly limited to such a plane and it is assumed that the primary beam is normal to the fibre axis. Consider a polycrystalline specimen in which part of the material is fibre oriented and the rest of it is randomly spaced. The frequency function, $N(\varphi)$, for a plane tending to parallelity with the fibre axis in such a case, has a maximum for $\varphi = 0$, i.e. for the equator on the reference sphere. The interference circle then has a pair of maxima on the equator of the X-ray diagram. We may further assume that the maxima do not overlap at the poles of the circle,

i.e. the total width of the peak on the frequency curve is less than $(\pi - 2\theta)$. If we plot the intensity I_α against the angle α we get for a full circle a diagram having two marked peaks and where the intensity values between the peaks are not zero.

As the intensity in any point of the interference circle may be considered as an additive function of contributions from each of the crystallites which reflect to that point, we may divide the intensity I_α into two parts

$$I_\alpha = I_{1\alpha} + I_{2\alpha}. \quad (8)$$

$I_{1\alpha}$ is due to the random part of the material, i.e. $I_{1\alpha}$ is the value between the peaks and $I_{2\alpha}$ is the intensity arising from the oriented material. The area under the α vs. I_α curve corresponds to the total amount of radiation scattered in the circle; the rectangular part at the bottom corresponds to the unoriented material and the area of the peaks to the oriented crystallites.

According to equation (6) we may write

$$N(\varphi) = k I_\alpha \cos \varphi \quad (9)$$

where k is a constant for this special interference. Further, applying equation (7), we have

$$\int_{\varphi_1}^{\varphi_2} N(\varphi) d\varphi = K \int_{\alpha_1}^{\alpha_2} I_\alpha \cos \alpha d\alpha \quad (10)$$

where

$$K = k \cos \theta.$$

In equation (10) the left member gives the part of the irradiated material, the normals of which (for the plane considered) intersect the reference sphere in the zone between the angles φ_1 and φ_2 . The limits of the integral to the right are the values of α corresponding to φ_1 and φ_2 and the integral gives the area between those limits under the curve which is obtained when $I_\alpha \cos \alpha$ is plotted against α .

If $N(\varphi)$ is divided into two parts in the same way as I_α , the fraction of oriented material, A (always referring to the plane considered) can be written (see appendix)

$$A = \frac{\int_{-\frac{\pi}{2}}^{+\frac{\pi}{2}} I_{2\alpha} \cos \alpha d\alpha}{\frac{2}{\cos \theta} I_{1\alpha} + \int_{-\frac{\pi}{2}}^{+\frac{\pi}{2}} I_{2\alpha} \cos \alpha d\alpha} \quad (11)$$

To simplify calculations equation (11) may be written in the more convenient form

$$A = \frac{1}{1 + \frac{c 2\pi I_{1\alpha}}{4 \int_0^{\frac{\pi}{2}} I_{2\alpha} d\alpha}} \quad (12)$$

where

$$c = \frac{2}{\pi \cos \theta \cos \xi} \quad (13)$$

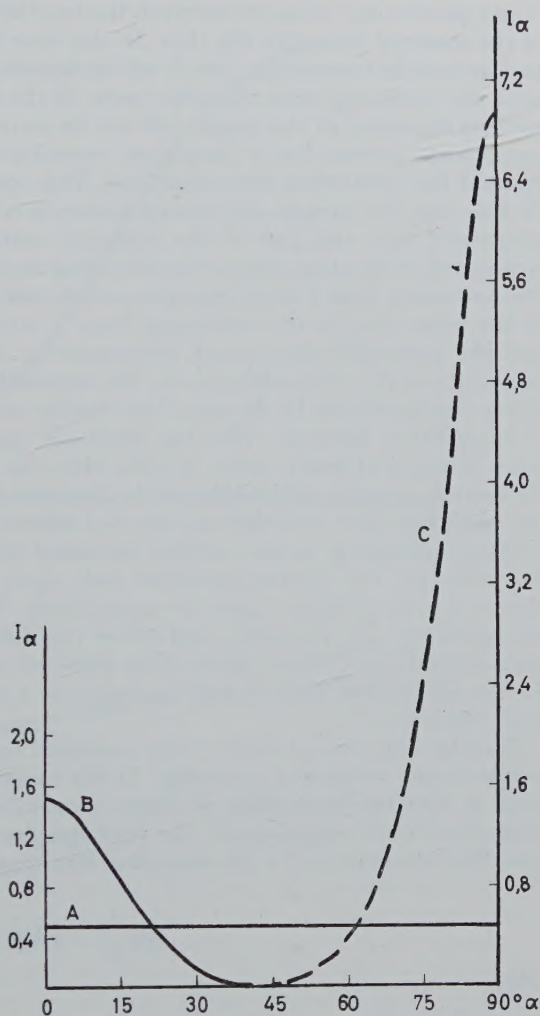
and ξ is an angle within the interval of α . If $N_2(\varphi)$ may be approximated by a Gaussian curve the value of $\cos \xi$ lies between 0.96 and 0.98 for peaks having a width at half

the total height between 15° and 35° (see appendix). It is easily seen that $4 \int_0^{\frac{\pi}{2}} I_{2\alpha} d\alpha$

corresponds to the radiation scattered by the oriented part of the material and that $2\pi I_{1\alpha}$ is due to the non-oriented material, both expressions referring to a full turn around the interference circle. As c may be determined, the proportion of oriented material can be graphically evaluated from measurements of the intensity distribution in an interference circle. From the same diagram of intensity distribution the sharpness of the orientation may also be estimated, according to well-known methods, by measuring the peripheral width of the peaks or by determining the integral width according to Laue. It is also seen that the values, here the fraction of oriented material and the sharpness of orientation, which could be used to characterize the state of orientation, should be independent of the intensity of the incident radiation and of the amount of irradiated material. This independence is an advantage from the experimental point of view. If the form of the peaks should be considerably different from the Gaussian curve assumed here (see appendix), the case should be subject to a special analysis and other values might be chosen to characterize the state of orientation. An intensity distribution of a different appearance is encountered in the spiral structures, an example of which will be treated in another connection.

Some orientation effects for planes, other than those oriented parallel to the fibre axis, may be briefly mentioned here. It is well known that fibre orientation of a specimen can give a marked increase in the intensity of an interference from a plane which is oriented normal to the fibre axis. Fig. 3 gives an example of this. It shows the intensity distribution, according to equation (6), along the interference circles from two different crystallographic planes, one of which is oriented mainly parallel to the fibre axis and the other normal to it. The constant k (equation (9)) and the function $N(\varphi)$ are assumed to be the same for both planes. The width at half the height for $N(\varphi)$ is assumed to be 36° and θ is 10° . In one case the maximum of $N(\varphi)$ lies at the equator of the reference sphere and in the other case the peak of $N(\varphi)$ is divided into two symmetrical halves the maxima of which are placed at the poles. The normal intersections corresponding to the plane oriented parallel to the fibre axis are distributed over the large zones near the equator, whereas the points corresponding to the plane oriented normal to the fibre axis are crowded into the narrow zones around the poles. Consequently, the density of the points corresponding to the plane oriented normal to the fibre axis will increase more towards the maximum than the density of the points corresponding to the other plane. The intensity variations may be useful but may also cause difficulties, as is well known, when the intensities are determined from diagrams taken with the usual powder cameras. For example, consider two reflections, A and B , having an intensity ratio $a:b$ for a non-oriented specimen, and assume that 10 % of the material in the specimen is fibre oriented. The crystallographic plane corresponding to A may be oriented parallel to the fibre and the plane corresponding to B normal to it. The distribution for each of the planes follows a Gaussian function $N(\varphi)$ having the width of the peak at half the height equal to about 60° . In this case the intensity ratio increases about 19 % at the

Fig. 3. Comparison between the intensity distribution in the interference circles corresponding to (A) a non-oriented plane, (B) a plane parallel to the fibre axis, and (C) a plane normal to the axis. The intensity is given in arbitrary units. It is assumed that the planes have the same scattering power and the same spacing. Further it is assumed that θ is 10° and that the distribution of the oriented planes follows the same Gaussian frequency curve having the width of the peak at half the height equal to 36° .



equator. For planes forming an oblique angle with the fibre axis the effect is not quite as large, but often larger than the percentage of oriented material. Obviously the effect is more pronounced for a sharper fibre orientation and vice versa.

In the preceding discussion the scattering from a polycrystalline material of mosaic crystals was considered without regard to the fact that high polymers usually contain a certain amount of amorphous material and that the crystallites may be quite different in size and perfection. It might be expected that the different states of order have different scattering power for a given angle θ , at least this ought to be the case for the amorphous material. These circumstances may cause difficulties. The amorphous material may scatter under such angles that the maxima in its

X-ray pattern are obtained between the interference circles from the crystalline part of the material (compare Fig. 1a). In this case the amorphous material disturbs the background determination, which will be described later, and further it is not recorded with the scattering from the other parts of the specimen. Thus, for such a case, the method discussed in this paper will not be convenient. It may also happen that the amorphous pattern has a maximum covering a crystalline interference which can be used for orientation determinations. This occurs for neoprene (compare Fig. 1b). In this case the background determination is not influenced as much as in the first-mentioned case and part of the radiation scattered from the amorphous material is recorded at the same time as the scattering from the crystalline part of the specimen. The scattering from a truly amorphous material cannot be ascribed to a certain plane in the same way as the scattering from a crystalline material. This circumstance and the previously mentioned differences in scattering power might not cause a large error in the value obtained for the orientation if the distribution of the different states of order should be the same both for the oriented and the non-oriented material. It is probable, however, that the randomly spaced part of the specimen contains more material of lower states of order than the oriented part and consequently the constant k (equation (9)) might not be the same for both parts of the specimen. From the preceding it is seen that uncorrected values for the amount of oriented material, obtained according to the method discussed here, are only approximate. Further, it is seen that the values depend not only upon the orientation in the specimen but also, to a certain degree, upon the crystallinity. For some materials, which crystallize on stretching (e.g. neoprene) and where the differences in crystallinity between the oriented and non-oriented parts of the material are very marked, the values obtained for the orientation may as well be taken as a relative measure of the crystallinity in the specimen.

Thus far only the intensity of the scattered radiation has been considered without regard to the method of recording. If the radiation is registered on a photographic plate or film the blackening of which is recorded with a microphotometer, circumstances are more complicated. The photographic method was used in this investigation. The blackening of a photographic film may be written

$$\log \frac{L_0}{L} = \gamma \log B \quad (14)$$

where

L_0 = the intensity of the incident light (in the photometer)

L = the intensity of the transmitted light

γ = the blackening constant

B = the exposure of the film.

In this case, B is equal to $t I_\alpha$ (t the exposure time), and with normal photographic processing γ should have a value near unity for the linear part of the logarithmic blackening curve. If the microphotometer gives a linear response to the incident light we may use the photometer readings S instead of the different values of L . Consequently we have for a point on the interference circle

$$\log \frac{S_0}{S_\alpha} = \gamma \log t \cdot I_\alpha. \quad (15)$$

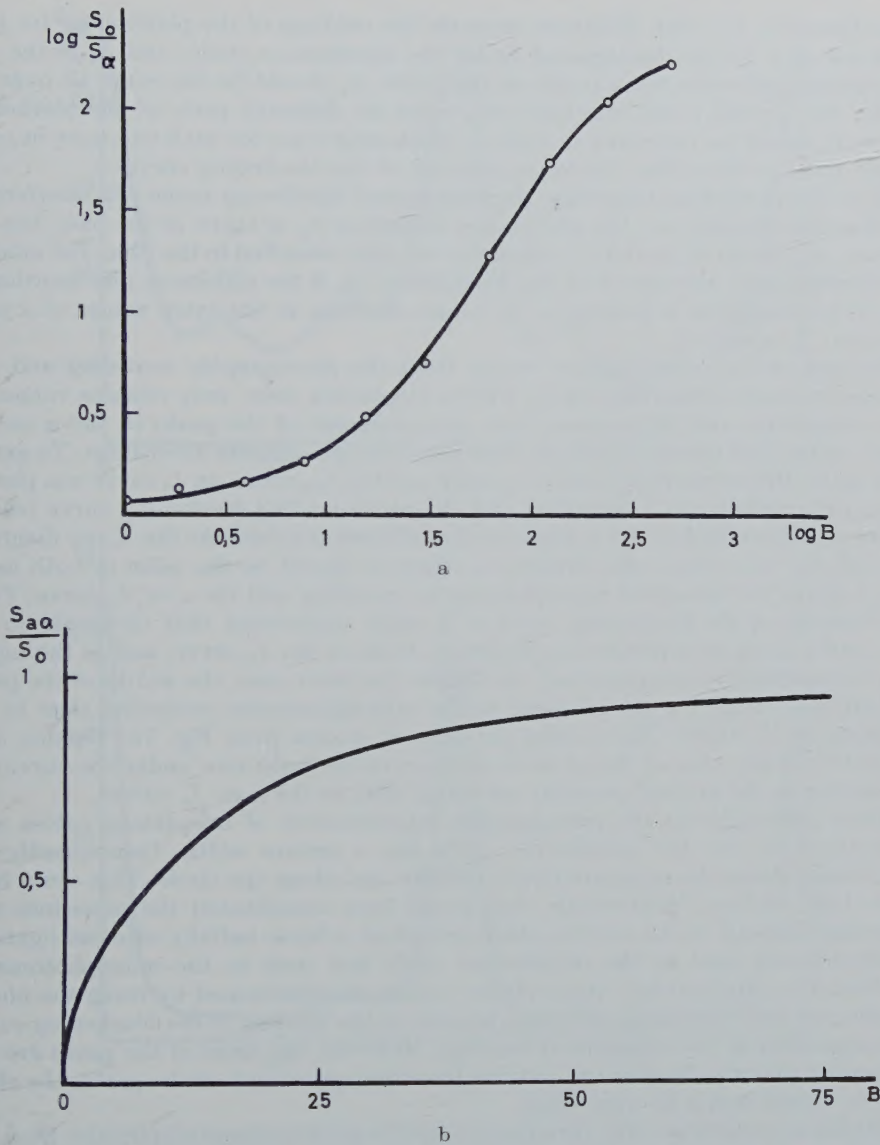


Fig. 4. The blackening curves, given in microphotometer deflections and in arbitrary exposure units.

S_0 the deflection corresponding to the incident light
 S_α " " " " " " transmitted light
 $S_{a, \alpha}$ " " " " " " absorbed light
 B the exposure

(a) The logarithmic blackening curve $\log (S_0/S_\alpha)$ vs. $\log B$.

(b) The fraction of absorbed light, $S_{a, \alpha}/S_0$, plotted against B . The curve in (b) is calculated from the curve in (a).

The deflection S_0 is the difference between the readings of the photometer for total darkness and for the background under the interference circle, and S_α is the corresponding difference for a point on the circle. S_0 should be the same all over the circle. As γ is not a real constant but varies for different parts of the blackening curve, it should be necessary to make a blackening scale for each exposure in order to get the I_α values. Fig. 4 gives an example of the blackening curves.

If, in the blackening recording, the background blackening under the interference circle in the diagram, i.e. the photometer deflection S_0 , is taken as the base, the difference, $S_{a\alpha}$, between S_0 and S_α represents the light absorbed in the film. The amount of absorbed light increases with the blackening, i.e. if the difference just mentioned, $S_{a\alpha}$, is considered as a function of α , we get maxima at the same values of α as in the α vs. I_α curve.

Because of the complications arising from the photographic recording and also because of some difficulties which will be mentioned later, only relative values for the orientation were determined from measurements of the peaks in the α vs. $S_{a\alpha}$ curve which was obtained directly from the microphotometer recordings. To get an idea of the differences between the I_α curve and the $S_{a\alpha}$ curve, an I_α curve was plotted from a microphotometer recording and the corresponding blackening curve (shown in Fig. 4). This was done for a diagram of a cellulose material. As the X-ray diagrams were of the same type, the differences observed should be the same in both cases. Fig. 5 shows the smoothed microphotometer recording and the α vs. I_α curve. From the bending of the blackening curve it is easily understood that the peaks in the $S_{a\alpha}$ curve must be depressed in relation to those of the I_α curve, and as the higher $S_{a\alpha}$ values decrease comparatively more than the lower ones, the widths of the peaks at half their heights must be larger in the microphotometer recording than in the constructed I_α curve. This is also the case as is seen from Fig. 5b. Further, it is obvious that the area of the peaks in relation to the total area under the curve will be smaller in the microphotometer recording than in the α vs. I_α curve.

Other difficulties in the photographic determination of orientation values arise from the fact that the interference circle has a certain width. Consequently the blackening should be integrated both radially and along the circle. This could have been done, at least theoretically, but would have complicated the procedure considerably. Instead, as the most practical procedure, a linear radially adjusted lightspot which covered most of the interference circle was used in the microphotometer. Further, it is obvious that when relative values are determined by using the photographic method, the values obtained, because of the bending of the blackening curve, also depend upon the exposure of the film. However, the areas of the peaks are less influenced than the heights and judging from the appearance of the peaks, the effect on the widths should be very small.

The background under the interference circle was determined empirically from two circular concentric microphotometer recordings; one on either side of the interference circle. The effects from incoherent scattering and air scattering were not specially taken into account. When the background recordings were taken, the linear lightspot was set parallel to the tangent to the interference circle. The circles, along which these recordings were taken, were determined from minima on the equatorial line of the X-ray diagram on both sides of the interference circle. The position of the background in relation to these recordings was estimated and averaged on some typical diagrams from recordings along the equator and along diameters at angles of 45° and 90° from the equator. On most of the diagrams only the circular recordings

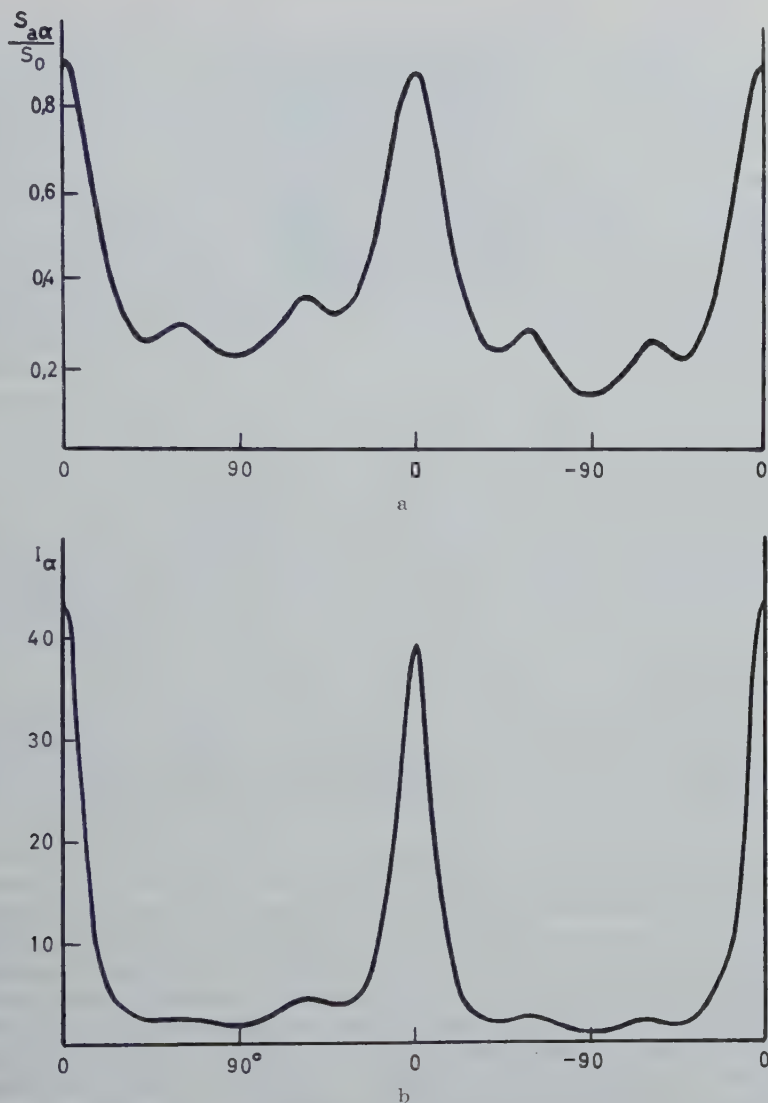


Fig. 5. (a) A smoothed-out microphotometer recording (for a cellulose specimen). (b) The recording in (a) plotted with intensities instead of "blackening" according to the curve in 4 (b). The intensity is given in arbitrary units.

The values of α are given along the x -axis with 0° at the equator and $+90^\circ$ and -90° at the poles. In the ideal case the ordinates should be the same in all points having the same value of $|\alpha|$.

were taken and the background determined according to the averaged relation. This choice of background may be questioned but it seemed to be the simplest way to get a background value directly from the X-ray diagram.

The preceding discussion may be summarized as follows. If it is assumed that oriented and non-oriented material scatter radiation in the same way, it is possible

to obtain graphically the percentage of oriented material, referring to a special plane, from the intensity distribution curve for the interference circle, corresponding to the plane considered, and having its maxima at the equator. A measure of the sharpness of the orientation may also be obtained from the same curve. The values obtained are independent both of the amount of material in the specimen and of the intensity of the primary beam. It is probable that in practice the first mentioned assumption does not hold and in that case the values are approximate. If the radiation is registered with a photographic method the determination of the intensity distribution curve is more complicated because of the bending of the photographic blackening curve. From direct measurements on the blackening recording for an interference circle it is possible to get relative values which may be used to characterize different specimens of the same material. Unfortunately, in this case the values obtained are dependent upon the exposure of the film, though it seems that within reasonable limits the exposure dependence is not very important. Thus, to avoid complications, an investigation of this kind should if possible be performed with the aid of equipment which permits the direct measurement of X-rays.

2. Orientation and elongation in polychloroprene

The materials investigated were two American samples, ANE and ANG, and two samples, Al 09 and Al 010, from Svenska Gummiforskningslaboratoriet (The Swedish Rubber Research Laboratory). Both Al 09 and Al 010 were polymerized in bulk. One of the American samples, ANE, was investigated both in the vulcanized and unvulcanized states, the others were not vulcanized. The vulcanization was made according to a standard formula. The vulcanizate contained about 22 % added ingredients, mainly magnesium oxide and zinc oxide, together 17 %, and 1 % sulfur. Some experiments were also made with some other Swedish materials to check that they fitted into the general scheme obtained in the experiments reported here.

Method

The unvulcanized materials were obtained as sheets or lumps and had been stored for at least one month when they were investigated. Pieces of about $20 \times 10 \times 2.5$ mm were cut from the interior of the material and from such a piece thin slices ($20 \times 2 \times 0.1$ mm) were cut with a simple microtome. Four to six slices were put together to form a specimen about 0.5 mm thick; the slices adhered to each other after the application of only slight pressure. This procedure was used to eliminate as far as possible inhomogeneities in the material. From the vulcanized sample which was macroscopically homogeneous a specimen with a thickness of 0.5 mm was directly cut. The specimen was clamped into a holder, and two marks were made on it about 5 mm apart. The distance between the marks was measured to a tenth of a millimeter and the specimen was stretched to the desired elongation with a screw arrangement. The specimens were exposed in an X-ray camera with a plane film at a distance of about 30 mm from the specimen, and with a pinhole system with a diameter of 1 mm. A Philips Metalix tube having a copper anode and provided with a nickel filter was used as the source of radiation. The load on the tube was 20 mA at 40 kV and the exposure time about 1 hour. All experiments were carried out at room temperature.

After processing the film, the blackening distribution along the interference circles was determined with a microphotometer which was built at the Institute. The light passing the film was measured with a light sensitive cell (a thermocouple or a selenium photoelement was used)

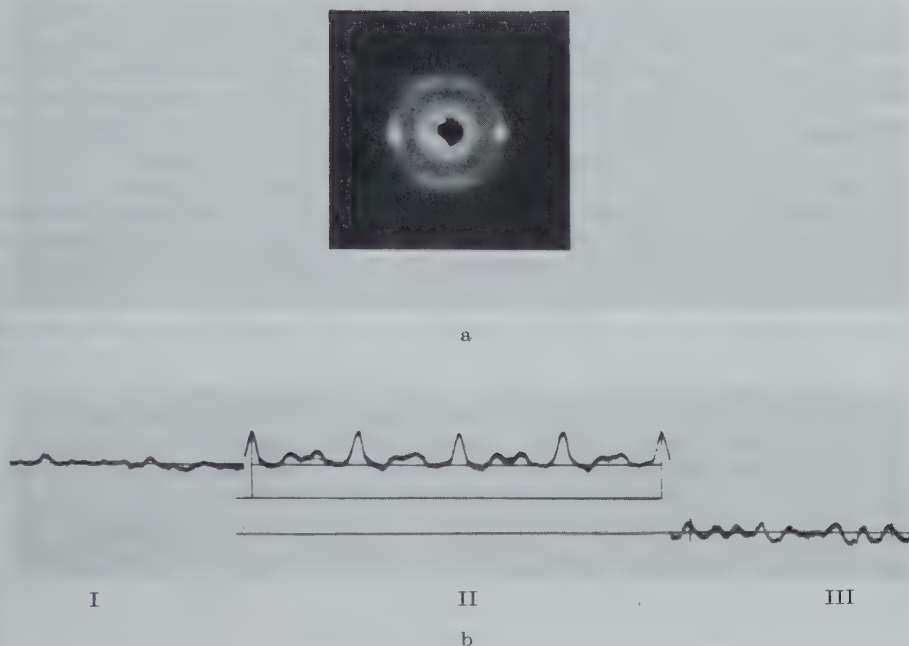


Fig. 6. (a) A neoprene diagram. Scale 1:1.5. (b) The corresponding circular microphotometer recordings with the background lines. Scale 1:4.5. I, The inner recording. II, The headcurve, two turns around the interference circle. III, The outer recording.

which operated upon a recording mirror galvanometer. As mentioned earlier, recordings were taken along the interference circle and along two other circles, one on each side of the interference. At the beginning all recordings were made in the same way, with rotation of the film (in its plane) and movement of the sensitive paper coupled (this method was used for most of the rubber diagrams), but later an arrangement was made which permitted a fast rotation of the film independently of the paper. With the film rotating at a speed of two to three turns per second the galvanometer could not follow but settled itself at a position which, as is easily seen, should correspond to the average blackening in the recorded circle. That the setting of the galvanometer really gave the average of the blackening was also checked experimentally. When this method was used the recording paper was placed on a rotating drum and when an average was recorded the drum was set so as to make the joint in the paper pass the lightspot from the galvanometer, thus giving a mark at both ends of the paper when it was taken off the drum. The interference circle was recorded in both ways because the recording of the average made the determination of the total area under the curve much easier; only the average was recorded for the blackening on both sides of the interference circle. An example of a diagram and the recordings is given in Fig. 6.

The treatment of the recordings was made as follows. If the average of the blackening on both sides of the interference had not been recorded directly, it was determined from straight lines drawn through the recorded curves in such a way that the areas between the curve and the line for one turn were the same on both sides of the line (a balancing line). From diametrical recordings

it was estimated that the probable background blackening for the interference was in the middle between the averages for the side recordings. A broken line then was drawn through all the minima of the recording of the interference circle (the headcurve) and the broken line was balanced with a straight line, which was taken as the boundary between the peaks and the bottom part of the area under the headcurve. The areas between the headcurve, or its average line, and the background and between the boundary line and the background were measured and the area of the peaks calculated from these measurements. The heights of the peaks were measured from the broken line and the widths of the peaks measured at half this height. As is seen from Fig. 6b there are six maxima on the headcurve, two large on the equator and four small corresponding to the first layer line. The areas of these small maxima have, mainly for practical reasons, been measured into the area of the peaks, though this is not quite correct.

It is seen from Fig. 1b that the interference ring at sufficiently high elongation may be split up into three different interferences. The three maxima on the equator, lying close to each other, seemed to have the same peripheral width and therefore no considerable error should be introduced by treating them as one interference. It would also have been difficult to get the intensity distribution of the strongest one in the middle without disturbances from the others and besides the separation of the interferences was not always observed. Of course an effect such as this coincidence of interferences complicates matters and renders the determination of absolute values uncertain. It is also seen from Fig. 6b that the recordings from which the background is determined are not quite smooth but have some more or less pronounced maxima and minima due to offshoots from the equatorial maxima or to the layer lines. In this case no corrections have been made for these irregularities. They ought to move the background slightly upwards and thus to a certain degree compensate some other previously mentioned effects which decrease the value for the relative amount of oriented material.

The diagrams of the vulcanized materials contained also some interference circles from the other recipe components and some of these circles showed orientation effects. As the nearest of these other interference circles had a radius about twice as large as the strongest neoprene circle the same method was used both for vulcanized and unvulcanized materials.

An estimation of the probable scattering of the values obtained showed that the total error due to the recordings of the blackening and the measurements on the recordings could be as high as 8%. To this must be added the previously discussed errors and also effects caused by inhomogeneities in the material. If all factors are taken into account it seems reasonable that the total spread of the measured values could amount to 15 to 20% which is about what was found in the experiments.

Results

Some spacings, d , obtained from the diagrams of unvulcanized materials (ANE and ANG) are given in Table 1. They are numbered from the center of the diagram.

Table 1. Spacings for unvulcanized materials.

No.	d Å	No.	d Å
1	9.19 ± 0.16	4	4.13 ± 0.06
2	4.95 ± 0.06	5	3.30 ± 0.03
3	4.45 ± 0.03	6	2.75 ± 0.03

The values given are the averages and the errors are calculated according to the expression $\Sigma|\delta|/n\sqrt{n-1}$; (δ = deviations from the average, n = number of diagrams measured). Numbers 1, 3, 5 and 6 were determined from ten diagrams and numbers 2 and 4 from five. The circle corresponding to number 1 was strong but broad and diffuse and might be composed of two or more interferences.

The period along the fibre axis was determined [14, 15] from six diagrams of unvulcanized materials. The average value found was 4.81 ± 0.01 Å. (It is believed that the accuracy in this case is somewhat fortuitous.)

The vulcanized material had a somewhat more diffuse pattern than the unvulcanized. Only the strongest interference circle from the polymer could be measured and the splitting of the equatorial maximum (spacings 2, 3 and 4) could not be observed. The interferences from the other components have not been measured systematically. The spacing corresponding to the strongest interference circle from the vulcanized neoprene was according to measurements on seven diagrams 4.42 ± 0.03 Å.

The result from the measurements on the orientation are given in Figs. 7 and 8. The elongation in per cent of the initial length of the specimen is plotted along the x -axis. In Fig. 8 the ordinate gives the area of the peaks in per cent of the total area under the headcurve and in Fig. 9 the ordinate gives the average, for one recording, of the peripheral widths of the peaks at half the height.

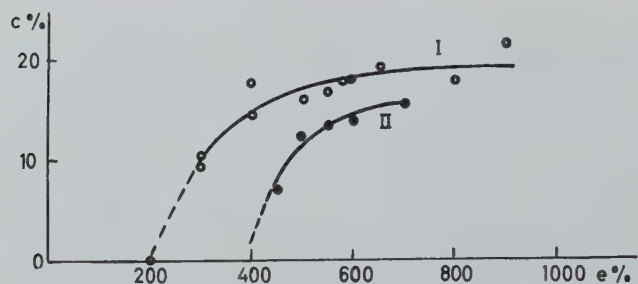
Discussion

The general tendency in all experiments is the same. At low elongations no difference from the unstretched material is observed in the diagrams, but when the elongation reaches a certain value, fairly sharp crystalline interferences appear and their intensity increases when the elongation is increased (Fig. 7). The crystallinity appears within a small interval of elongation. Fig. 7 also shows that the orientation, after the first appearance of the crystalline interferences, at the beginning increases practically linearly with the elongation. From the preceding discussion of the method it is seen that this does not necessarily mean that the amount of organized material also increases linearly, but it is probable that the deviation from linearity is not very large. When the elongation has reached values somewhere between 400 and 600 per cent the curve for the orientation bends off towards a limiting value or even goes down for higher elongation.

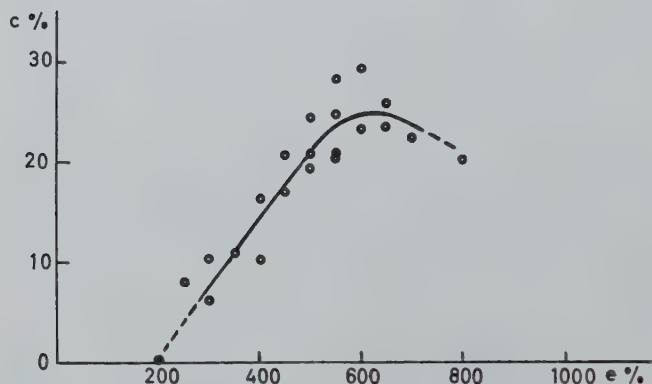
From Fig. 8 it is seen that the width of the peaks measured along the interference circle, with one exception, has a slight tendency to decrease when the elongation is increased. The discussion of the method shows that this effect in reality must be larger than that found from the measurements as the height of the peaks increases with the elongation and consequently the previously mentioned increase of the width (see above, page 208) measured directly on the microphotometer recording must be more pronounced at higher elongations. However, the parallelity of the crystallites is very marked even at lower elongations.

The sudden appearance of crystalline interferences, the approximately linear growth of crystallinity with the elongation, the bending of the curve at higher elongations and the sharpness of orientation are also well known from X-ray experiments on natural rubber (e.g. [1, 3, 16]).

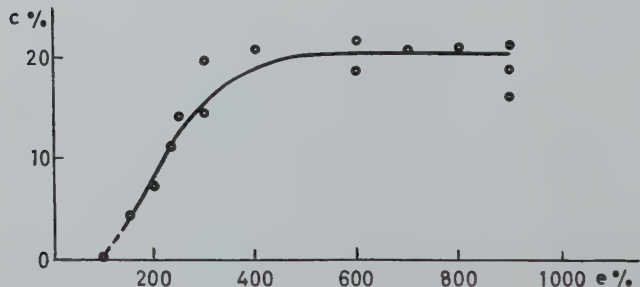
The decrease of the peripheral width of the maxima is probably due to a sharper



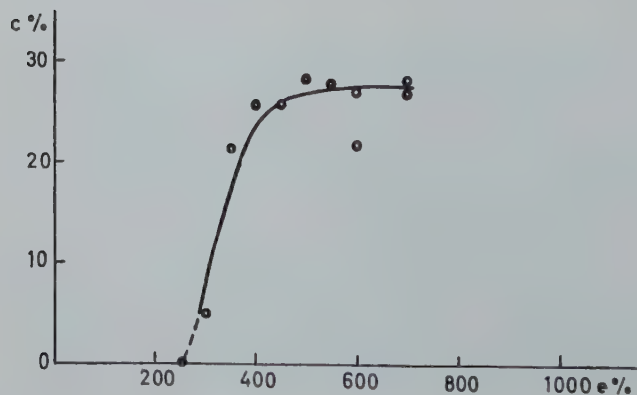
(7 a) ANE. I, The specimens were stretched and exposed. II, The specimens were stretched 500 %, relaxed and within a few minutes stretched again and exposed. The elongation in this case is given in relation to the length of the specimen before the first stretching.



(7 b) ANE vulcanized.



(7 c) ANG.



(7 d) Al 09.

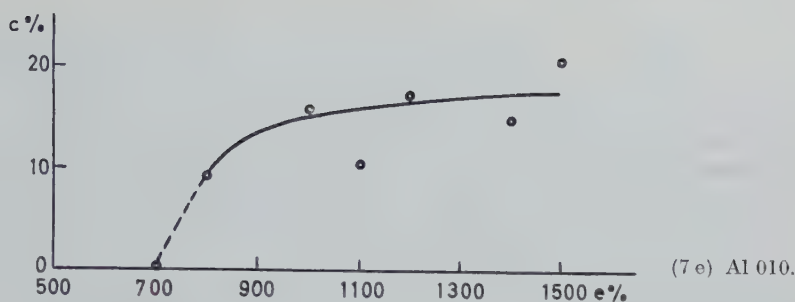


Fig. 7. The values for the crystallinity (orientation), c , plotted against the elongation, e .

orientation of the crystallites. The radial width of the crystalline interferences has not been systematically measured but from the microphotometer recordings taken along the equator it seemed that the width was practically constant. Of course the previously mentioned widening effect for higher degrees of blackening comes in here too but it is probably safe to conclude that the crystallites are of about the same order of magnitude at the different elongations.

When the specimen is stretched the molecular chains must be oriented but this effect obviously is not large enough to be observed on the diffuse halo. In the case of unvulcanized materials, at least, there is probably also a plastic flow in the material which permits the molecules to coil up again but not enough to neutralize the effect of the stretching. As this is continued the chains are better lined up and at a certain elongation the forces causing crystallization overcome the thermal movements and part of the material arranges itself in a crystal lattice. The elongation at which this takes place, for natural rubber, has been called the critical elongation [16] and this term, for shortness, will also be used here. It is well known that the critical elongation for natural rubber depends not only upon the material but also upon the treatment of the specimen (e.g. preheating [3]). This is also the case for neoprene as is seen from Fig. 7a. The limiting value of the orientation is also influenced by the treatment (Fig. 7a). The effect upon the critical elongation may in this case partly be explained by a plastic flow in the material, as the elongation for the lower curve was measured in relation to the length of the specimen before the first stretching, but the lowering of the limiting value can hardly be explained in this way. When these effects are taken into consideration it is obvious that the preparation of the specimen must be carefully standardized if the values of the critical elongation or the maximum value of orientation are to be used to characterize the materials. From this point of view it might be questioned if the procedure adopted here, i.e. storing of the materials at room temperature for at least one month, is satisfactory. This procedure was chosen as some of the materials were quite different in solubility and other properties.

The question of how the growth of crystallinity takes place at elongations larger than the critical value cannot be answered from the experiments. As mentioned above it seems that the crystallites have about the same sizes at the different elongations, but still it is quite possible that the linear dimensions of the crystallites increase some ten per cent or even more during the stretching and this of course means a considerable increase in the volume of the crystallites already formed. However, it is also possible that there are formed imperceptible nuclei of crystallization, during

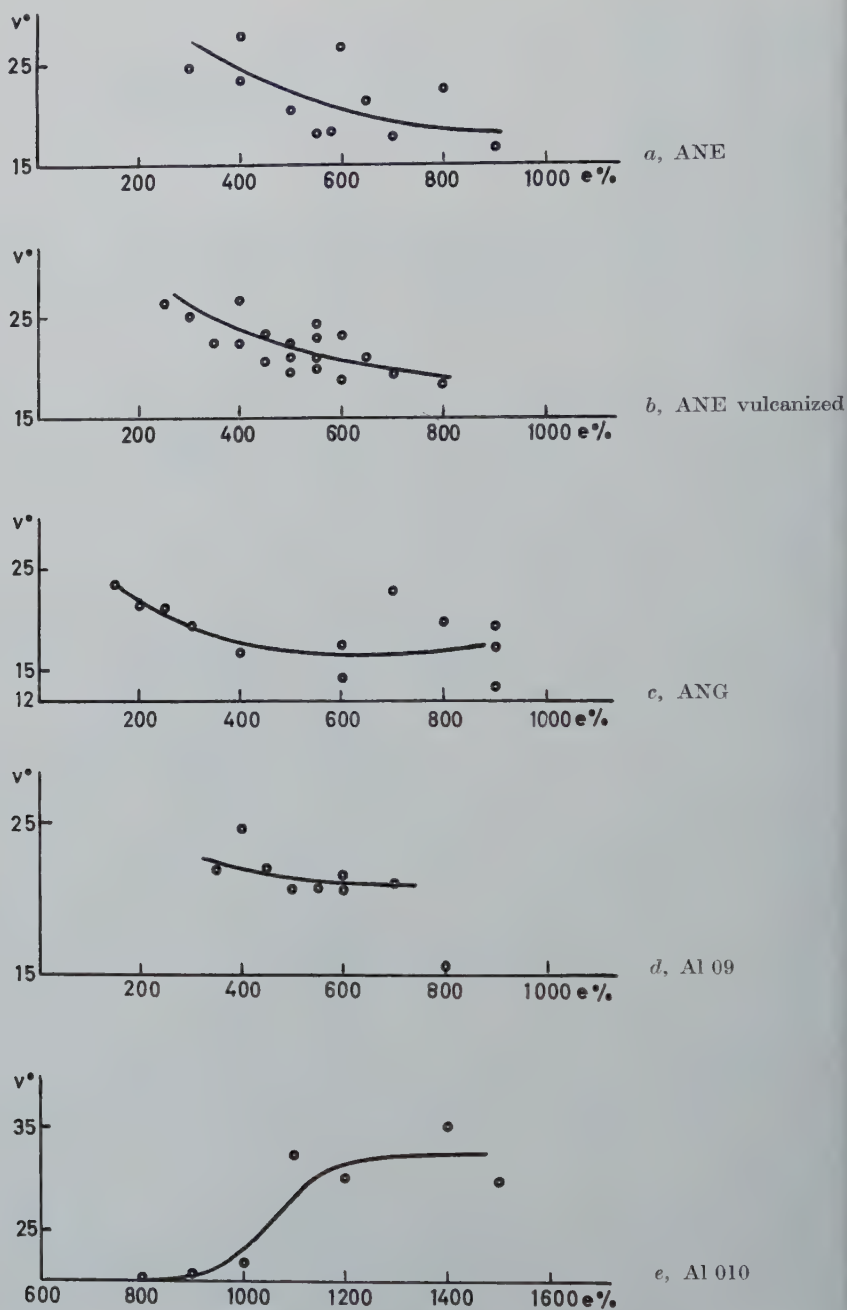


Fig. 8. The angular width, v (in degrees), of the equatorial maxima at half the height plotted against the elongation.

the earlier stages of elongation, which grow on subsequent stretching, or that there are formed new crystallites at the different elongations.

The bending of the curve of crystallinity at higher elongations has also been found for natural rubber [3] and may be explained by a flow in the material when the tension becomes high enough. In the case of vulcanized ANE, where the curve seems to have a maximum at about 600 % elongation and reaches a higher value of crystallinity than the curve for the unvulcanized specimen, it was found from the mechanical tests on the material, that it broke at about the same elongation. In the X-ray experiments it was not possible to stretch the vulcanized specimens more than about 800 %, i.e. not far beyond the maximum on the curve, because the material broke. The higher value of the crystallinity for the vulcanized ANE as compared with the unvulcanized material is probably due to the cross-linking which prevented plastic flow and thus allowed a higher tension in the specimen. It therefore seems to be a probable explanation of the maximum of the curve for the vulcanized material, that some chains or cross-linkages or both were disrupted at the higher elongations which caused a decrease of the strain and the orienting forces in the material. The bending down effect may, though it seems quite reasonable, be uncertain, as it is based essentially only on two measurements; the higher crystallinity for the vulcanized material seems to be safely established. This is further confirmed by the measurements on Al 09 for which higher values of crystallinity were found than for any other material. Al 09 was practically insoluble in the usual solvents and could not be worked on rollers in the rubber mill because it broke up into small fragments which shows that it consisted mainly of a polymer which had been cross-linked already during the polymerization, i.e. it should behave in the same way as a vulcanized material.

From Fig. 7 it is seen that the slope of the linear parts of the curves for ANE, vulcanized ANE and ANG is approximately the same but that Al 09 differs from the others—Al 010 is not taken into consideration here. It is also evident that there are fairly large differences between the critical elongations for the different materials. As mentioned earlier the critical elongation, at least partly, depends upon the treatment of the specimen and it is probable that this dependence is due to small changes in the structure, for instance the destruction or formation of nuclei of crystallization. However, the experiments do not permit any definite conclusions to be drawn regarding the connection between the properties of the material on one side and on the other the critical elongation and the slope of the curve.

The polymer Al 010 was different in many ways from the others investigated here. It was very soft and plastic at room temperature, not very elastic even after vulcanization and allowed extremely high elongations without breaking. As is seen from Fig. 7 the scatter of the values for the orientation (crystallinity) is larger than for the other materials but yet it is seen that the general form of the curve is the same. The critical elongation was in this case without any doubt very high as several exposures were taken at elongations about 500 to 600 per cent which showed no sign of crystalline interferences or orientation. Another peculiarity which is easily seen in the curve in Fig. 8e is that the width of the peaks along the circle increases considerably at the higher elongations. A similar effect may also be traced in the curve for ANG in Fig. 8c. As pointed out before no systematic measurements were made on the radial width of the interferences but visually no radial broadening of the interferences could be observed. The increase of the peripheral width of the peaks for Al 010 is much larger than the errors in the measurements and shows that at

the higher elongations the crystallites were at least partly preserved but that their parallelity decreased. This decrease may be due to plastic flow in the material and the fact that the sharpness of the interferences in the radial direction was practically unchanged shows that in this case the forces causing a breakdown of the crystallites were not considerably stronger than the forces keeping the molecules together in a lattice when once this had been formed. In this respect there seems to be a similiarity with racked natural rubber. Much work was not done on materials like Al 010, and it was the only one of this type which was investigated by X-rays. It has been mentioned here as an example of the plastic products which have also been obtained in the polymerization of chloroprene.

Some attempts to get higher orientation in neoprene specimens, according to the procedure of Gehman and Field [17], have also been made but gave no results whereas the same experiments with raw natural rubber gave diagrams showing higher orientation. It may not be impossible to get higher orientation in neoprene but, at least, it is much more difficult than to get higher orientation in natural rubber.

According to the experiments reported here there are large similarities, with regard to the properties investigated, between neoprene and natural rubber. There seem to be some differences, e.g. higher value for the critical elongation for neoprene than for natural rubber, the difficulties to get higher orientation in neoprene and possibly also a comparatively higher crystallinity in vulcanized neoprene materials than in vulcanized natural rubber [3]. Still the agreement between the curves obtained for natural rubber and for neoprene is very marked.

APPENDIX

(Unless otherwise stated the notations here are the same as in the main text.)

A. The intensity in a fibre diagram

Consider a fibre specimen with the frequency function $N(\varphi)$ for the positions of a given crystallographic plane in the specimen. The number of points within a zone $d\varphi$ on the reference sphere is equal to $n_0 N(\varphi) d\varphi$. A randomly oriented specimen with the same number of crystallites and consequently with the same total number of points, will have a number of points within the zone $d\varphi$ which is equal to $n_0 \cos \varphi d\varphi$. If the number of crystallites is large enough to permit the use of an average volume for each of them, which is a fairly safe assumption, the volume of the scattering material in a specimen is proportional to the number of points on the reference sphere. Therefore the ratio of the number of points in the zone $d\varphi$ for the random and for the oriented specimen is the same as the ratio of the corresponding intensities.

For the intensity I of a random material we have according to equation (5)

$$I = I_0 p Q V \frac{\cos \theta}{4\pi} \quad (5)$$

and consequently the intensity I_α at a point α on the interference circle for the fibre oriented specimen can be written

$$I_\alpha = \frac{I_0 p Q V \cos \theta N(\varphi)}{2\pi \cos \varphi} \quad (6)$$

The angle α along the interference circle corresponds to the angle φ on the reference sphere according to the relation

$$\sin \alpha = \frac{\sin \varphi}{\cos \theta} \quad (7)$$

Equation (6) also involves the assumption, which is probably not quite as safe as the one first mentioned, that the scattering power is the same for all parts of the specimen.

A rough estimation of the number of crystallites involved in the scattering of radiation, to show that the number is sufficiently high to permit the use of an average, can be made as follows. In X-ray work of this kind the specimens usually have dimensions of at least 0.1 mm in each direction and the crystallites may have dimensions of 1000 Å or less. If the packing is such that the volume of the crystallites is 20 % of the volume of the specimen there are 2×10^8 crystallites (cubes) in the specimen. If the material is randomly oriented the intersections between the normals of the planes in the crystallites and the sphere are evenly distributed over the reference sphere, and the probability that a plane lies in position for reflection is equal to the area of the zone of reflection divided by the area of the sphere. The angular width of the zone of reflection may be of the order of 1° and if the zone lies at a distance of 75° from the primary beam, which corresponds to an angle θ of 15° , the total number of crystallites in position for reflection is about 1.7×10^6 , and if we take an element of about 2° of the interference circle there are about 10^4 crystallites reflecting to that element. This number is probably a lower limit and may for ordinary work be at least ten times higher.

A derivation of equation (6) could, of course, also be made from the definition of the integral reflection and would make it possible to estimate the errors due to the width of the interference, but it is somewhat longer and the preceding derivation gives enough information for the present purposes.

B. The determination of the amount of oriented material

The frequency function $N(\varphi)$ may be split up into two parts in the same way as I_α , cf. equation (8).

$$N(\varphi) = N_1(\varphi) + N_2(\varphi),$$

where $N_1(\varphi)$ corresponds to the non-oriented part of the material and $N_2(\varphi)$ to the oriented part. From equation (1) it follows that

$$\int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} [N_1(\varphi) + N_2(\varphi)] d\varphi = 1.$$

The fraction, A , of oriented material (referring to the plane considered) can be written

$$A = \frac{\int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} N_2(\varphi) d\varphi}{\int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} [N_1(\varphi) + N_2(\varphi)] d\varphi} = \frac{\int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} N_2(\varphi) d\varphi}{1}.$$

It was assumed that the intensity maxima were so narrow that they were completely separated from each other on the interference circle, i.e. the value of $N_2(\varphi)$ is zero for $\varphi \geq (\pi/2 - \theta)$. Consequently the fraction of oriented material should be proportional to the integral

$$\int_{-\pi/2}^{+\pi/2} I_2 \alpha \cos \alpha d\alpha \quad (\text{according to (10)}). \quad \text{Thus}$$

$$A = \int_{-\frac{\pi}{2}}^{+\frac{\pi}{2}} N_2(\varphi) d\varphi = K \int_{-\frac{\pi}{2}}^{+\frac{\pi}{2}} I_{2\alpha} \cos \alpha d\alpha,$$

where K is the constant factor.

The fraction of non oriented material, $(1 - A)$, can be written in a similar way using the other part of the frequency function. Thus we have

$$(1 - A) = \int_{-\frac{\pi}{2}}^{-\frac{\pi}{2}} N_1(\varphi) d\varphi.$$

In this case the integral $\int_{-\pi/2}^{+\pi/2} I_{1\alpha} \cos \alpha d\alpha$ is proportional only to that part of the non-oriented material for which the normals intersect the reference sphere within a zone the limits of which are $\varphi = -(\pi/2 - \theta)$ and $\varphi = +(\pi/2 - \theta)$. As the points corresponding to the non-oriented material are evenly distributed over the sphere it is possible to correct the expression for the non-oriented material.

$$\int_{-(\frac{\pi}{2}-\theta)}^{+(\frac{\pi}{2}-\theta)} N_1(\varphi) d\varphi = \frac{4\pi \cos \theta}{4\pi} \int_{-\frac{\pi}{2}}^{+\frac{\pi}{2}} N_1(\varphi) d\varphi = K \int_{-\frac{\pi}{2}}^{+\frac{\pi}{2}} I_{1\alpha} \cos \alpha d\alpha$$

and

$$(1 - A) = \int_{-\frac{\pi}{2}}^{+\frac{\pi}{2}} N_1(\varphi) d\varphi = \frac{K}{\cos \theta} \int_{-\frac{\pi}{2}}^{+\frac{\pi}{2}} I_{1\alpha} \cos \alpha d\alpha.$$

As A can be written $A/\{(1 - A) + A\}$ and remembering that $I_{1\alpha}$ should be constant we now obtain

$$A = \frac{\int_{-\frac{\pi}{2}}^{+\frac{\pi}{2}} I_{2\alpha} \cos \alpha d\alpha}{\frac{2}{\cos \theta} I_{1\alpha} + \int_{-\frac{\pi}{2}}^{+\frac{\pi}{2}} I_{2\alpha} \cos \alpha d\alpha} \quad (11)$$

This equation can be written in a more convenient form because $I_{2\alpha}$ is assumed to be symmetric with respect to the equator ($\varphi = 0$).

$$A = \frac{1}{1 + \frac{2 \cdot I_{1\alpha}}{2 \cos \theta \cos \xi \int_0^{+\frac{\pi}{2}} I_{2\alpha} d\alpha}}$$

where ξ is an angle within the interval of α . The expression $4 \int_0^{\pi/2} I_{2\alpha} d\alpha$ is equal to the area of the peaks for a full turn around the interference circle and the corresponding area for the non-oriented material is equal to $2\pi I_{1\alpha}$. If these expressions are put into the preceding formula we get

$$A = \frac{1}{1 + \frac{c 2\pi I_{1\alpha}}{4 \int_0^{\pi/2} I_{2\alpha} d\alpha}} \quad (12)$$

where

$$c = \frac{2}{\pi \cos \theta \cos \xi} \quad (13)$$

The areas $2\pi I_{1\alpha}$ and $4 \int_0^{\pi/2} I_{2\alpha} d\alpha$ may be determined directly from the intensity distribution curve (the α vs. I_α curve) for the interference circle, and $\cos \xi$ may be estimated from the width of the peaks.

From the form of the maxima in the α vs. I_α curve it seemed reasonable to approximate the distribution function for the oriented part of the material ($N_2(\varphi)$) as a Gaussian curve ($N_2(\varphi) = (h\sqrt{\pi}) \exp(-h^2\varphi^2)$, h a constant). In investigations of this kind those parts of the Gaussian curve for which the ordinate is less than 1% of the maximum may be neglected. In this special case, concerning the rubber specimens, where the width of the peaks at half the maximum height usually varied from about 15° to 35° , it was found from graphical measurements that $\cos \xi$ varied from about 0.98 to 0.96. These values are comparatively rough estimations, and the assumption of a Gaussian distribution may not be the best approximation, but still it is seen that c , with a reasonable accuracy and within fairly wide limits, may be considered as a constant. If it is necessary $\cos \xi$ may easily be estimated for wider peaks or with better accuracy.

(Compare the appendix with [12, 13].)

Summary

For a simple fibre-oriented specimen the intensity distribution in an interference circle corresponding to a plane parallel to the fibre axis has been derived as a function of the orientation in the specimen. Based upon the intensity distribution an expression, referring to a plane parallel to the fibre axis, has been calculated for the amount of oriented material in the specimen.

A method has been described by which it is possible to get the relative amount of oriented material in a fibre specimen from a photographic X-ray diagram. The method involves the use of a microphotometric recording of the blackening along an interference circle corresponding to a plane parallel to the fibre axis. Elongation-orientation (crystallinity) curves have been determined for some neoprene materials according to the method described.

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Tryckt den 5 september 1956

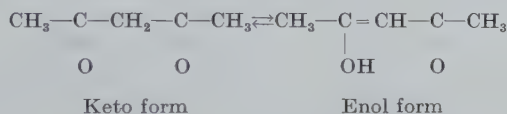
Uppsala 1956. Almqvist & Wiksells Boktryckeri AB

Proton magnetic resonance in acetylacetone and its keto-enol equilibrium

By B. N. BHAR

With 1 figure in the text

We have observed the resolved proton magnetic resonance spectrum of acetylacetone ($\text{CH}_3\text{COCH}_2\text{COCH}_3$) by the application of the high resolution nuclear magnetic resonance method with a view to determine the keto-enol equilibrium. The application of the high resolution nuclear magnetic resonance for the determination of the keto-enol equilibrium in a tautomeric mixture was first suggested and applied by Jarrett, Sadler and Shoolery (1). Their result of the keto-enol form of acetylacetone (2,4 pentanedione) however was not in close agreement with the value determined by the well-known Kurt Meyer bromine titration method. The equilibrium of the keto and enol forms of acetylacetone can be chemically represented as follows:



The migration of a proton from the CH_2 group of the keto form to associate with oxygen to form a hydroxyl group in the enol form gives rise to four groups of chemically non-equivalent protons in the tautomeric mixture, viz. protons in CH_3 , CH_2 , CH and OH groups, and hence it is possible to observe four chemically shifted proton magnetic resonance lines. Thus, by measurement of areas of selected peaks, the keto and enol content can be determined.

The spectrum of these chemically shifted lines in a magnetic field of approximately 4930 gauss is presented in Fig. 1. The principle and technique of experimental observation is practically the same as described in a previous communication (3). The resonance absorption signals are plotted against magnetic field which, in the diagram, increases linearly from left to right. The magnetic field is swept through the resonance at a rate of approximately 4 milligauss/sec. The experiment was done at the temperature of the room, which was kept constant at 25°C .

The proton signal of the OH group of the enol form, marked 1, occurs at the lowest value of the externally applied magnetic field, since the diamagnetic shielding of protons in the OH group is lower than the other three groups. The diamagnetic shielding of protons in the $\text{C}=\text{CH}-\text{C}$ group being generally less than protons in the CH_2 group, the peak 2 is from the CH group of the enol form and peak 3 is from the CH_2

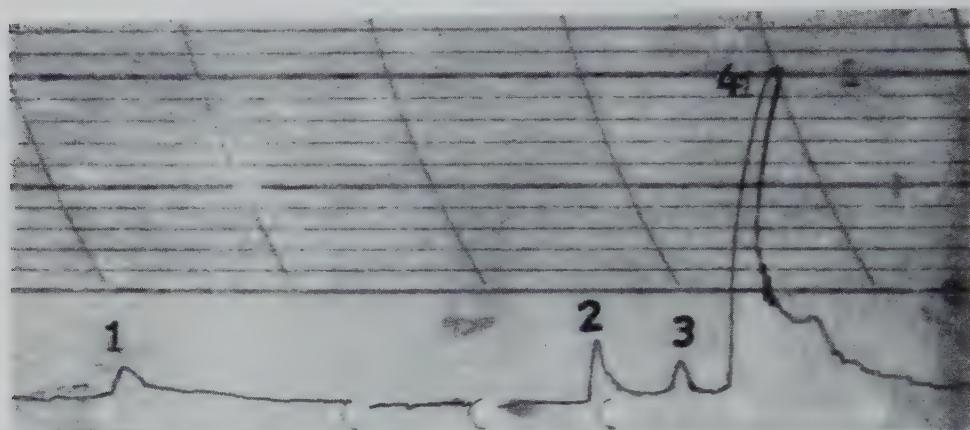


Fig. 1. The resolved proton signals from acetylacetone. The assignment of the peaks to different chemical groups is explained in the text. The total sweep width is 100 milligauss.

group of the keto form. Moreover the areas under peak 1 and peak 2 being approximately equal, they must represent signals from groups which contain an equal number of protons, and hence they must arise from the OH and CH groups of the enol form. Peak 4 represents the proton signal from methyl groups of both keto and enol form. To determine the keto and enol form we have compared the areas under peak 1 of the enol form with half the area under peak 3 and have found that the enol content is 75 % and the keto form is 25 %, which closely agrees with the value 76 % and 24 % respectively as given by the bromine titration method.

The difference of Jarrett, Sadler and Shoolery's value for the keto-enol distribution from that of the bromine titration method is possibly due to the fact that the rate at which the magnetic field was swept through the resonance was not slow enough, as a result of which the signal from the CH_2 group of the keto form, one of the peaks selected for area measurements, was appearing when the wiggles (4) from the peak of the CH_3 group had not completely died down. Moreover, in their case the peak of the enolic CH was also followed by wiggles. The enolic OH peak, however, was not followed by wiggles, possibly due to different transversal relaxation times. The possibilities of having different relaxation times of non-equivalent nuclei in a molecule have recently been discussed by Bloch (5). We want to stress that for the selection of peaks for area measurements they should not be associated with wiggles arising from the relaxation mechanism and rapidity of the change of magnetic field through resonance. Considering this point it is better to select the OH peak which was free from such transient oscillations. In our case the rate of change of the magnetic field was 4 milligauss/sec, which was sufficiently slow not to give rise to wiggles. It seems that for the determination of the keto-enol equilibrium in a tautomeric mixture by the high resolution nuclear magnetic resonance, one of the essential criteria should be a very slow sweep rate so as not to give rise to wiggles with the chemically shifted nuclear magnetic signals.

I wish to express my grateful thanks to Professor Manne Siegbahn, Director of the Institute, for his kind hospitality. I also wish to thank Docent G. Lindström for his advice and encouragement in our work.

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Uppsala 1956. Almqvist & Wiksells Boktryckeri AB

On the isomorphous replaceability of the cyano group by halogens and by the hydroxyl group in benzoic acid

By GÖRAN CLAESON

With 12 figures in the text

The mutual isomorphous interchangeability of fluorine, chlorine, bromine, iodine and hydroxyl group in substituted benzoic acid has been carefully studied. Lettré found (1) that the different chlorobenzoic acids formed continuous series of mixed crystals with the corresponding bromobenzoic acids and iodobenzoic acids. The same system of mixed crystals was also formed between bromobenzoic acids and the corresponding iodobenzoic acids. The hydroxyl group, however, could not isomorphically replace any of the three halogens. The phase diagrams of the hydroxybenzoic acids and chloro- (bromo-, iodo-) substituted acids exhibited simple eutectic points. Porath and Claeson have shown (2) that the three fluorobenzoic acids form solid solutions to a limited extent with both the corresponding chloro and the hydroxy acids. The fluorine compounds thus occupy an intermediate position between the chloro and the hydroxy compounds.

Very little is known about the possibility of isomorphous substitution for the cyano group by the halogens and by the hydroxyl group. Rheinboldt has found (3) that the cyano group in aromatic linkage is sometimes capable of such a replacement. He studied the following binary liquid-solid phase diagrams.

$2\text{-C}_{10}\text{H}_7\cdot\text{CN} + 2\text{-C}_{10}\text{H}_7\cdot\text{F}$	V	(75 %)
$2\text{-C}_{10}\text{H}_7\cdot\text{CN} + 2\text{-C}_{10}\text{H}_7\cdot\text{Cl}$	complete miscibility	
$2\text{-C}_{10}\text{H}_7\cdot\text{CN} + 2\text{-C}_{10}\text{H}_7\cdot\text{Br}$		(18 %)
$2\text{-C}_{10}\text{H}_7\cdot\text{CN} + 2\text{-C}_{10}\text{H}_7\cdot\text{J}$		(32 %)
$p\text{-O}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CN} + p\text{-O}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{F}$	Simple eut.	
$p\text{-O}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CN} + p\text{-O}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{Cl}$	IV	(44 %)
$p\text{-O}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CN} + p\text{-O}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{Br}$	V	(77 %)
$p\text{-O}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CN} + p\text{-O}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{J}$	Simple eut.	
$o,p\text{-(O}_2\text{N)}_2\text{:C}_6\text{H}_3\cdot\text{CN} + o,p\text{-(O}_2\text{N)}_2\text{:C}_6\text{H}_3\cdot\text{OH}$	Simple eut.	
$o,p\text{-(O}_2\text{N)}_2\text{:C}_6\text{H}_3\cdot\text{CN} + o,p\text{-(O}_2\text{N)}_2\text{:C}_6\text{H}_3\cdot\text{F}$	V	(30 %)
$o,p\text{-(O}_2\text{N)}_2\text{:C}_6\text{H}_3\cdot\text{CN} + o,p\text{-(O}_2\text{N)}_2\text{:C}_6\text{H}_3\cdot\text{Cl}$	V	(57 %)
$o,p\text{-(O}_2\text{N)}_2\text{:C}_6\text{H}_3\cdot\text{CN} + o,p\text{-(O}_2\text{N)}_2\text{:C}_6\text{H}_3\cdot\text{Br}$	V	(73 %)
$o,p\text{-(O}_2\text{N)}_2\text{:C}_6\text{H}_3\cdot\text{CN} + o,p\text{-(O}_2\text{N)}_2\text{:C}_6\text{H}_3\cdot\text{J}$	Simple eut.	

The figures IV and V denote the types IV and V of Bakhuis-Roozeboom's classification, and the figures in brackets denote the miscibility gap in the solid state.

The present author has studied the binary liquid-solid phase systems having either *m*- or *p*-cyanobenzoic acid as one component. *o*-Cyanobenzoic acid decomposes when heated, and therefore it could not be included in this investigation.

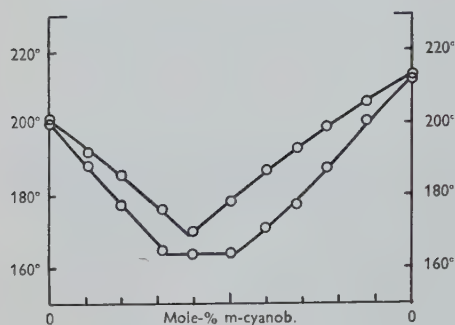


Fig. 1. *m*-Hydroxybenzoic acid + *m*-cyanobenzoic acid.

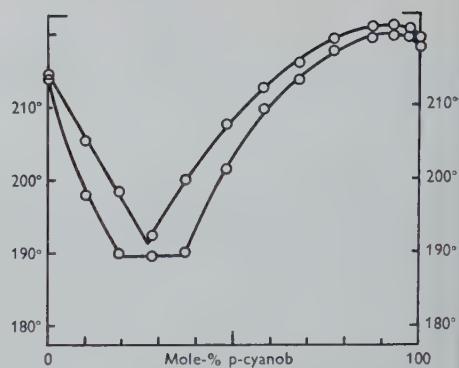


Fig. 2. *p*-Hydroxybenzoic acid + *p*-cyanobenzoic acid.

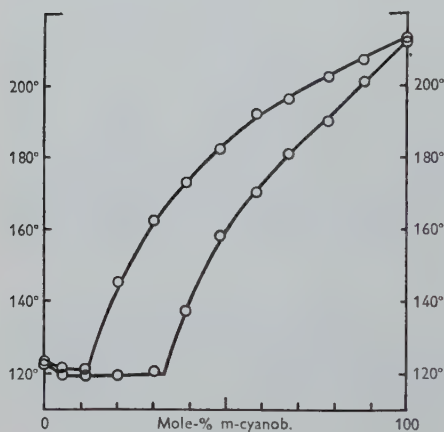


Fig. 3. *m*-Fluorobenzoic acid + *m*-cyanobenzoic acid.

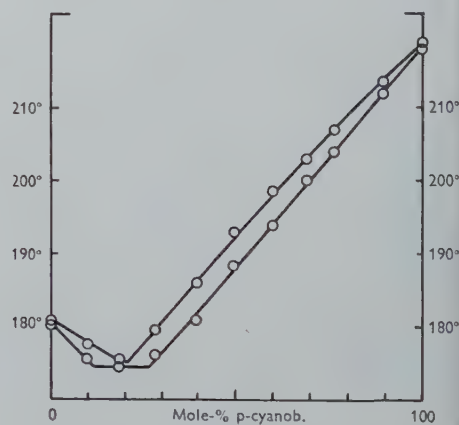


Fig. 4. *p*-Fluorobenzoic acid + *p*-cyanobenzoic acid.

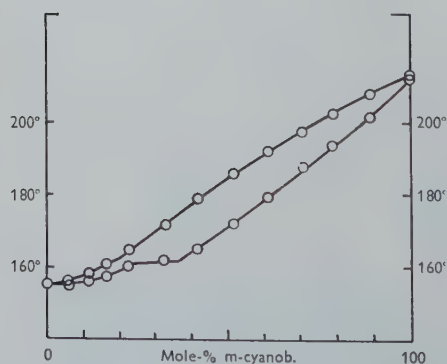


Fig. 5. *m*-Chlorobenzoic acid + *m*-cyanobenzoic acid.

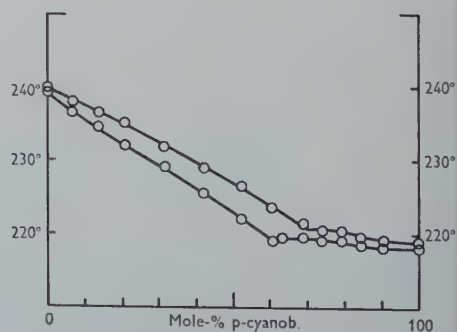
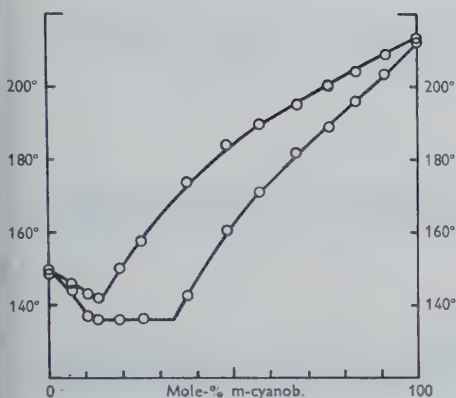
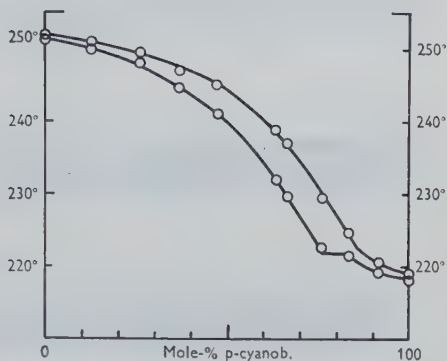
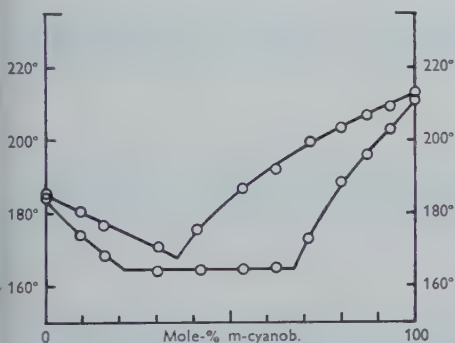
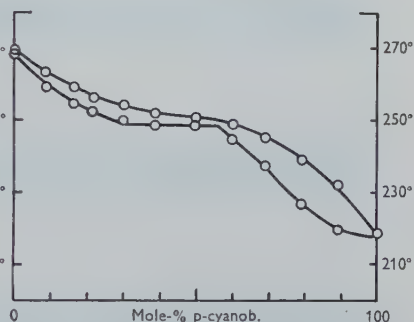


Fig. 6. *p*-Chlorobenzoic acid + *p*-cyanobenzoic acid.

Fig. 7. *m*-Bromobenzoic acid + *m*-cyanobenzoic acid.Fig. 8. *p*-Bromobenzoic acid + *p*-cyanobenzoic acid.Fig. 9. *m*-Iodobenzoic acid + *m*-cyanobenzoic acid.Fig. 10. *p*-Iodobenzoic acid + *p*-cyanobenzoic acid.

In all of the investigated systems, limited formation of mixed crystals is obtained. Figs. 1, 3, 4, 7 and 9 give diagrams of the type V of Roozeboom, with a more or less pronounced miscibility gap. The diagrams shown in Figs. 5, 6, 8 and 10 differ slightly from the preceding ones—all exhibiting peritectic points and being of the type IV of Roozeboom. Fig. 2, representing the phase diagram of *p*-hydroxybenzoic acid mixed with *p*-cyanobenzoic acid, is of the type V of Roozeboom. In the right-hand part of the diagram, however, the melting-point curve passes through a slight maximum. X-ray powder photographs of different compositions of the two components show that a line distribution appears in the vicinity of 90 % *p*-cyanobenzoic acid which is quite different from both that of *p*-cyanobenzoic acid and that of *p*-hydroxybenzoic acid (cf. Fig. 11). It seems clear that the acids form a molecular compound, at about this composition. This was also verified by means of Kofler's microscopic contact method (4). Possibly the molecular compound is formed in the ratio 1:7.

It appears from the diagrams that all of the mixtures give solid solutions to a limited extent. Even fluorine, iodine and hydroxyl are partly interchangeable with the cyano group, which is not the case in some of Rheinboldt's investigations. This

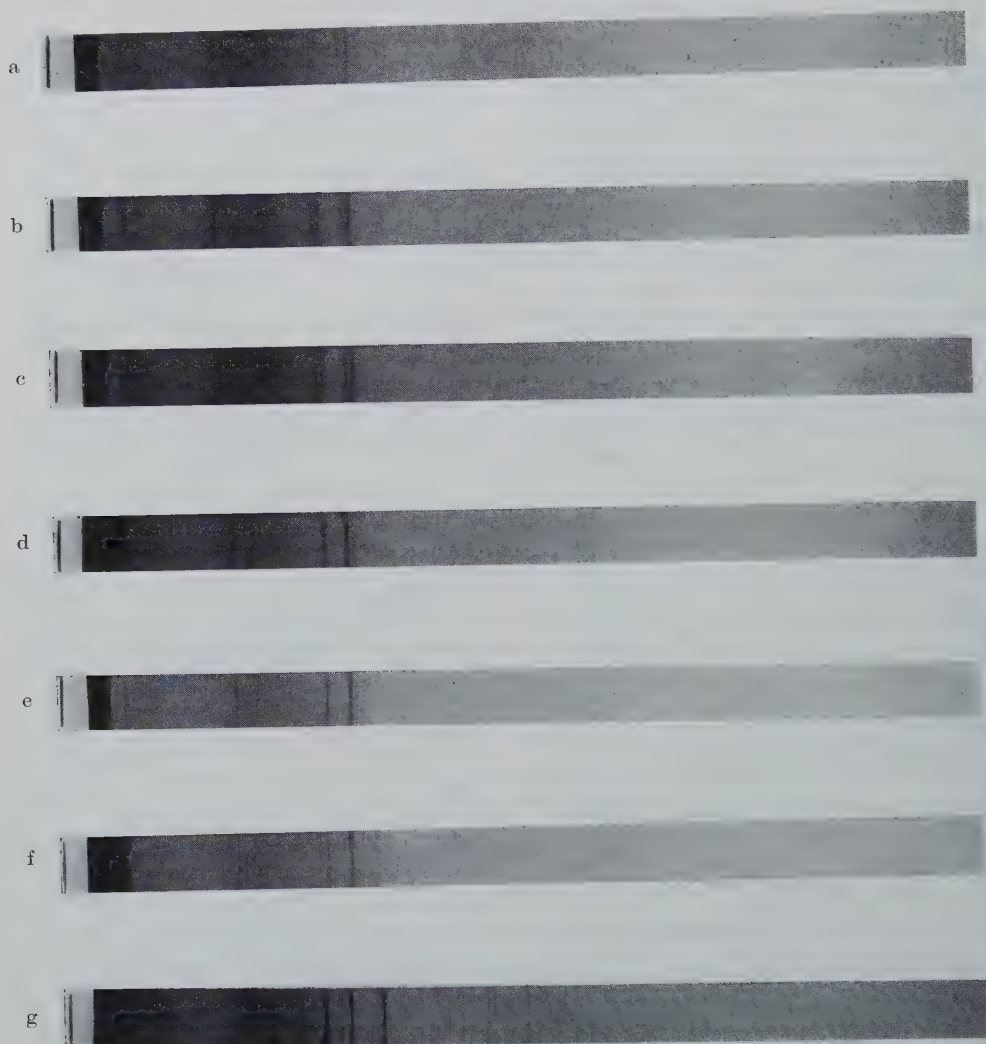


Fig. 11.

a	<i>p</i> -Cyanobenzoic acid				
b	95,4 % <i>p</i> -cyanobenzoic acid +	4,6 %	<i>p</i> -hydroxybenzoic acid		
c	93,8 %	"	" + 6,2 %	"	"
d	87,7 %	"	" + 12,3 %	"	"
e	67,6 %	"	" + 32,4 %	"	"
f	48,1 %	"	" + 51,9 %	"	"
g	<i>p</i> -Hydroxybenzoic acid				

fact illustrates the observation that the isomorphous replaceability of one group by another is not a generally applicable rule, but must, for certainty, be studied separately for each organic system.

One also notes that the chloro- and bromobenzoic acids have the smallest miscibility gap with the corresponding cyanobenzoic acids. The iodo and cyano compounds

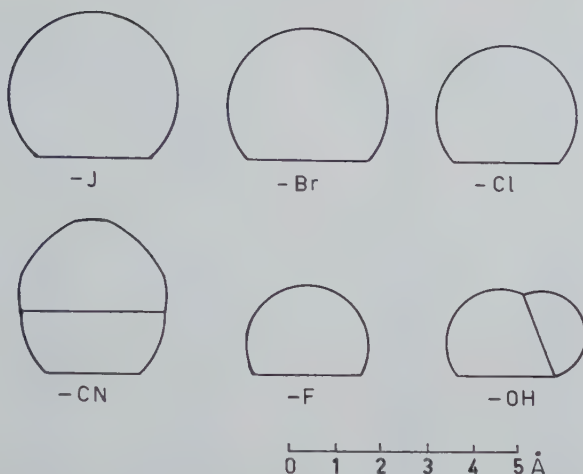


Fig. 12. Spheres of action (from BRIEGLEB).

are least soluble in each other. This is in good agreement with Rheinboldt's finding that the crystal-chemical affinity between an aromatic cyano compound and the corresponding halo compound decreases regularly from the chlorine to the bromine to the iodine derivative.

Probably the isomorphous replaceability of an atom or a group by another is a function of both the polar character and the space requirement. It is instructive to compare the atomic models in question. One will see from Fig. 12 that the radius of the sphere of action of the cyano group lies intermediate between those of the chlorine and bromine. The data for the spheres of action are those given by Briegleb (5).

It is also worth noting that in all the cases studied, the para-isomers have a less pronounced miscibility gap than the meta-isomers.

Experimental

The preparation of the acids used for the melting-point determinations

m-Cyanobenzoic acid was prepared from *m*-aminobenzoic acid (6) and recrystallized first from hot water and then from 50 % acetone. M.p. 212–213.5°.

p-Cyanobenzoic acid was prepared from *p*-aminobenzoic acid (6) and crystallized from hot water and several times from 25 % alcohol. M.p. 218–219°.

m-, and *p*-Hydroxybenzoic acids, *m*-, and *p*-fluorobenzoic acid and *m*- and *p*-chlorobenzoic acids were obtained according to the methods of Porath and Claeson (2).

m-Bromobenzoic acid was obtained through bromination of benzoic acid (7) and recrystallized several times from acetone and water. M.p. 148.5–150°.

p-Bromobenzoic acid "Eastman" was recrystallized from benzene. M.p. 253–254°.

m-Iodobenzoic acid was obtained from *m*-aminobenzoic acid (8) and recrystallized from acetone and water. M.p. 184.5–185.5°.

p-Iodobenzoic acid was prepared from *p*-aminobenzoic acid (9). The acid was sublimed and crystallized from 50 % alcohol. M.p. 268–269.5°.

Table 1. *m*-Hydroxybenzoic acid and *m*-cyanobenzoic acid.

Mole-% <i>m</i> -cyano- benzoic acid	Thawing point	Melting point
0	200.5	201.5
10.7	188.5	192.5
19.9	178.0	186.0
31.1	165.0	176.5
39.5	164.0	170.0
50.0	164.0	178.5
59.8	171.0	187.0
68.3	177.5	193.0
76.6	187.5	199.0
87.7	200.5	206.0
100	212.0	213.5

Table 2. *p*-Hydroxybenzoic acid and *p*-cyanobenzoic acid.

Mole-% <i>p</i> -cyano- benzoic acid	Thawing point	Melting point
0	213.0	214.5
10.0	198.0	205.5
19.2	190.0	198.5
28.1	198.5	192.5
37.2	190.0	200.0
48.1	201.5	207.5
58.1	209.5	212.5
67.6	213.5	216.0
76.9	217.5	219.0
87.7	219.5	221.0
93.8	219.5	221.0
97.3	219.5	220.5
99.1	218.0	219.0
100	218.0	219.0

Table 3. *m*-Fluorobenzoic acid and *m*-cyanobenzoic acid.

Mole-% <i>m</i> -fluoro- benzoic acid	Thawing point	Melting point
0	122.5	123.5
5.1	119.5	121.5
11.4	119.0	121.5
20.4	119.5	145.5
30.2	120.5	162.5
39.3	137.5	173.0
48.8	158.0	182.5
58.8	170.0	192.0
67.4	181.0	196.0
78.6	190.0	202.5
88.2	201.0	207.0
100	212.0	213.5

Table 4. *p*-Fluorobenzoic acid and *p*-cyanobenzoic acid.

Mole-% <i>p</i> -cyano- benzoic acid	Thawing point	Melting point
0	180.0	181.5
9.9	175.5	177.5
18.3	174.5	175.5
28.2	176.0	179.5
39.5	181.0	186.0
49.5	188.5	193.0
58.9	194.0	198.5
69.1	200.0	203.0
76.6	204.0	207.0
89.8	212.0	213.5
100	218.0	219.0

Phase diagrams

Weighed amounts of the components (total weight 10 mg) were dissolved in a few drops of acetone ("Anala R" standards for laboratory chemicals). The solvent was evaporated at room temperature and the residues were carefully powdered and dried in a desiccator. The melting point determinations were performed by Rheinboldt's method (10) with melting point capillary tubes in an electrically heated melting point apparatus. In the case that sublimation occurred, the tube was sealed just above the sample. A calibrated thermometer was used. Owing to the occurrence of sublimation, it was difficult to use a hot-stage microscope.

Table 5. *m*-Chlorobenzoic acid and *m*-cyanobenzoic acid.

Mole-% <i>m</i> -cyano- benzoic acid	Thawing point	Melting point
0	155.0	155.5
5.8	155.0	156.0
11.7	156.5	158.0
16.7	157.5	161.0
22.7	160.0	164.5
32.6	162.0	171.5
41.5	165.0	179.0
51.4	172.0	186.0
61.0	179.5	192.5
70.4	187.5	197.5
78.9	193.5	202.5
89.1	201.5	208.0
100	212.0	213.5

Table 6. *p*-Chlorobenzoic acid and *p*-cyanobenzoic acid.

Mole-% <i>p</i> -cyano- benzoic acid	Thawing point	Melting point
0	238.5	240.0
6.9	236.5	238.0
13.9	234.5	236.5
20.9	232.0	235.0
31.9	229.0	232.0
42.1	225.5	229.0
52.6	222.0	226.5
60.6	219.0	223.5
63.5	219.5	222.5
69.3	219.5	221.5
73.9	219.0	220.5
79.7	219.0	220.5
84.3	218.5	219.5
90.7	218.0	219.0
100	218.0	219.0

Table 7. *m*-Bromobenzoic acid and *m*-cyanobenzoic acid.

Mole-% <i>m</i> -cyano- benzoic acid	Thawing point	Melting point
0	148.5	150.0
6.3	144.0	146.0
10.9	137.0	143.0
13.6	136.0	142.0
19.4	136.0	150.0
25.2	136.5	157.5
37.6	142.5	173.5
48.3	160.5	184.0
57.3	171.0	189.5
67.2	182.0	195.0
76.0	189.0	200.5
83.4	196.0	204.0
91.7	203.5	209.0
100	212.0	213.5

Table 8. *p*-Bromobenzoic acid and *p*-cyanobenzoic acid.

Mole-% <i>p</i> -cyano- benzoic acid	Thawing point	Melting point
0	253.0	254.0
12.7	250.0	251.0
25.8	248.0	249.5
36.9	244.5	247.0
47.2	241.0	245.0
63.2	232.0	239.0
66.4	229.5	237.0
76.0	222.5	229.5
83.4	221.5	224.5
91.7	219.0	220.5
100	218.0	219.0

In the determination of the phase diagram between *p*-iodobenzoic acid and *p*-cyanobenzoic acid, the liquid phase became dark-coloured. For that reason, the melting points were hard to determine, and the curve is a little uncertain.

X-ray photographs

Powder photographs were taken with CuK_α radiation (45 kV, 22 mA) using a camera of the Guinier type (11). The exposure time was six hours. The preparations were obtained in the same manner as described for the determination of the melting point diagrams.

Table 9. *m*-Iodobenzoic acid and *m*-cyanobenzoic acid.

Mole-% <i>p</i> -cyano- benzoic acid	Thawing point	Melting point
0	184.5	185.5
9.5	174.0	180.5
16.1	168.5	177.0
30.5	164.0	171.0
42.1	164.5	175.5
53.7	164.5	187.0
62.5	165.0	192.0
71.4	173.0	199.5
80.1	188.5	203.5
87.1	196.0	207.0
93.3	203.0	209.5
100	212.0	213.5

Table 10. *p*-Iodobenzoic and *p*-cyano-
benzoic acid.

Mole-% <i>m</i> -cyano- benzoic acid	Thawing point	Melting point
0.0	268.0	269.5
9.6	259.0	263.5
16.7	254.5	259.0
21.5	252.5	256.5
29.9	250.0	254.5
38.9	249.0	252.0
50.0	249.0	251.0
60.2	245.0	249.0
69.3	237.5	245.0
79.1	227.0	238.5
89.5	220.0	232.0
100.0	218.0	219.0

Summary

The isomorphous replaceability of the cyano group by the halogens and by the hydroxyl group has been studied by means of ten binary solid-liquid phase diagrams. It has been shown that *m*-, and *p*-cyanobenzoic acids, to a limited extent, form solid solutions with the corresponding hydroxy-, fluoro-, chloro-, bromo- and iodo-benzoic acids. The phase diagrams are of the types IV and V of Roozeboom. The diagram for *p*-cyanobenzoic acid and *p*-hydroxybenzoic acid exhibits a peculiarity in forming a molecular compound at about 90 % *p*-cyanobenzoic acid.

The author wishes to express his thanks to Professor Arne Fredga for valuable advice and discussions, and to Dr. Sigvard Wideqvist who kindly placed the cyanobenzoic acids at his disposal.

Department of Organic Chemistry, Chemical Institute, University of Uppsala, February 1956.

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Uppsala 1956. Almqvist & Wiksells Boktryckeri AB

Use of countercurrent distribution for the identification of aldosterone (Δ^4 -pregnene-21-ol-3,20-dione-18-al)

By HANS CARSTENSEN

With 2 figures in the text

Chemical as well as biological determination of aldosterone in biological material require its separation from companion steroids, especially cortisone and cortisol, which may interfere with the test methods. For analytical purposes this has been carried out by previous investigators with paper partition chromatography using systems devised by Bush and by Zaffaroni (1, 2). In preparative work similar systems have been employed for chromatography on cellulose, kieselguhr (2) and silica gel (3) columns.

The order of movement is different in the two types of systems. Simpson and Tait used the systems of Bush containing benzene, benzene + ethyl acetate or toluene + ethyl acetate as mobile phase and aqueous methanol as stationary phase. Here aldosterone moved between cortisone and cortisol. In the system of Zaffaroni, containing propylene glycol/toluene, aldosterone moved slightly faster than cortisone. They were not separated in the usual 24-hour chromatograms although complete separation was reported after seven days (4, 5).

From an examination of the literature it would appear that the separation of aldosterone from cortisone and cortisol has in no case been accomplished in the same system. Paper chromatography seems to be somewhat more efficient than chromatography on partition columns, although a direct comparison is difficult as R_F values are lacking. From the partition coefficients (α) calculated for the three steroids from experiments on kieselguhr columns (4) it would appear that the maximal separation factor for aldosterone-cortisol was 1.8 (obtained in the system benzene/50 % methanol + 50 % water) and that for aldosterone-cortisone 1.6 (obtained in the system 90 % benzene + 10 % ethyl acetate/50 % methanol + 50 % water).

Some disadvantages connected with the chromatographic methods may be avoided in the Craig liquid-liquid countercurrent distribution (6) which provides a more reliable method for determining the partition coefficient as a physical constant of the molecule. Countercurrent distribution studies of the common adrenocortical steroids have shown that all of them may be adequately separated, at least for identification purposes, in suitable biphasic solvent systems by as few as 24 transfers (7, 8). Later on, when aldosterone was made available it was therefore of interest to investigate its partition characteristics in some of the systems previously applied to the other corticosteroids.

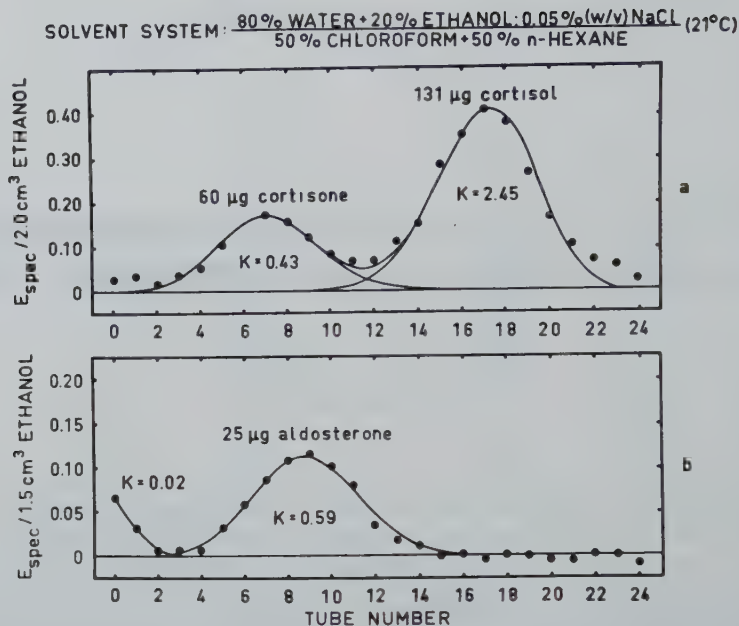


Fig. 1. Countercurrent distribution curves ($n = 24$) of cortisone and cortisol (a) and of aldosterone (b) in the same solvent system from experiments carried out simultaneously. The corrected ultra-violet extinction values (E_{spec}) of the fractions are represented by solid circles. Theoretical curves are represented by solid lines and correspond to the K values given.

Experimental

The methods employed for this investigation are identical with those previously reported (8).

Optimal separation between cortisol and cortisone was reported (8) in a system containing 80 % water + 20 % ethanol; 0.05 % (w/v) NaCl/50 % chloroform + 50 % *n*-hexane.¹ The means of five determinations of the partition coefficients, K , were 2.58 for cortisol and 0.50 for cortisone (separation factor $\beta = 5.2$). In the present experiment the aldosterone sample was run in the same system parallel with a mixture of cortisone and cortisol, using 24 transfers in each experiment (temperature 21°C). After evaporation of the solvents in nitrogen under reduced pressure, the contents of each tube were dissolved in distilled ethanol and read at 225, 240 and 255 $m\mu$ in a Beckman spectrophotometer Model DU. The results after base-line correction according to Allen (cf. 8) are illustrated in Fig. 1. Two components appeared in the aldosterone experiment. The main one gave $K = 0.59$. This is assumed to be identical with authentic aldosterone. The total quantity was estimated to be 25 μg using data published by Simpson, Tait, Wettstein, Neher, v. Euw and Reichstein (9) for calculation of ϵ_{spec} for aldosterone² ($\epsilon_{\text{spec}} = 14,175$). The smaller, less polar component with $K = 0.02$ was about 13 % of the total specific extinction. This is

¹ The composition of the biphasic systems is described by the volumes used for each phase.

² ϵ_{spec} is defined as the molar extinction coefficient after base line correction according to Allen using the wavelengths stated in each case. E_{spec} is defined as the actual specific extinction coefficient after similar correction.

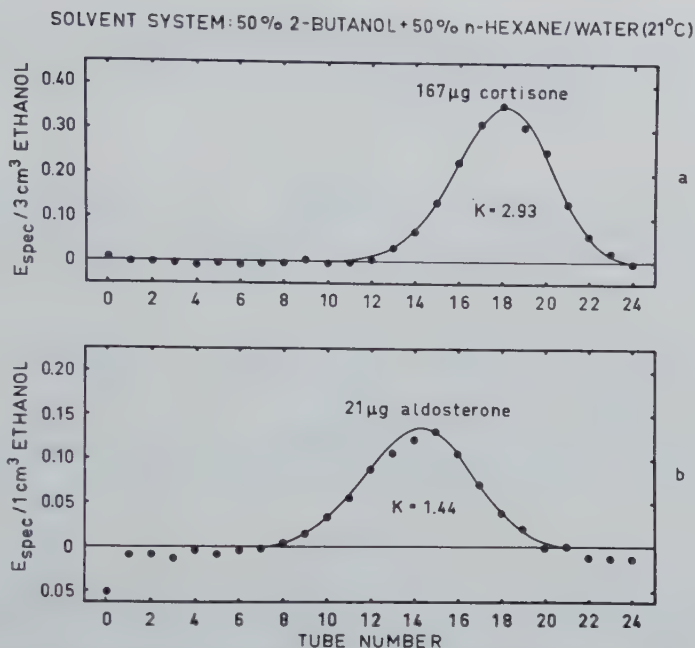


Fig. 2. Countercurrent distribution curves of cortisone (a) and aldosterone (b) in the same solvent system from experiments carried out simultaneously. For further explanation cf. Fig. 1.

probably an artifact or possibly a contaminant, although the aldosterone sample might have been one of the purest available.¹ Owing to the strong separation between the two components, it is highly improbable that they would have resulted through a separation of the aldehyde form from the cyclohemiacetal form of aldosterone. The separation factors calculated from the data of these experiments were 1.4 for aldosterone/cortisone and 4.2 for cortisol/aldosterone. Thus the system is suitable only for a separation of the latter pair. With equal amounts an almost complete separation of cortisol and aldosterone is obtained using about 50 transfers.

For the attempt then to separate cortisone and aldosterone it was primarily of interest to try systems containing 2-butanol, *n*-hexane and water as some steroids behaved irregularly in these, e.g. reversed order and complete separation of Δ^4 -pregnene-17 α ,21-diol-3,20-dione and Δ^4 -pregnene-21-ol-3,11,20-trione (7). The main peak in the previous experiment with aldosterone was collected and distributed in parallel with cortisone in the system 50% 2-butanol + 50% *n*-hexane/water at 21°C (Fig. 2). Aldosterone now gave $K = 1.44$ and cortisone $K = 2.93$ ($\beta = 2.0$). The K value of cortisol had been determined previously (7), being 2.83. It is therefore seen that the order of aldosterone on one side and cortisol-cortisone on the other side is reversed in this system. Although the separation obtained is not complete (unless using about 200 transfers) this system may be of value in the characterization and partial separation of aldosterone from both cortisol and cortisone.

¹ The sample of aldosterone was produced by Dr. A. Wettstein, Basle, and investigated by infrared spectrography at King Gustaf V Research Institute, Stockholm, by Dipl. Engineer L. Plantin who afterwards placed it at my disposal. I wish to thank him sincerely for this generous gift.

Another system containing 2-butanol and *n*-hexane was also tried without giving better separation between aldosterone and cortisone. Using 65 % 2-butanol + 35 % *n*-hexane/water the following *K* values were obtained: aldosterone 3.5, cortisone 6.7 (duplicates), Δ^4 -pregnene-21-ol-3,11,20-trione 8.

Conclusions

Aldosterone may be separated from cortisol adequately for identification purposes in a 24 and completely in a 50 transfer countercurrent distribution at 21°C using the solvent system 80 % water + 20 % ethanol; 0.05 % (w/v) NaCl/50 % chloroform + 50 % *n*-hexane.

Using about 200 transfers, the simultaneous separation of aldosterone from cortisone and cortisol would be possible with countercurrent distribution in the solvent system 50 % 2-butanol + 50 % *n*-hexane/water at 21°C.

Identification of aldosterone in a mixture of steroids will be possible with the use of a combination of a few 24 transfer countercurrent distributions in different solvent systems described in the present and a previous communication (8).

Summary

The partition characteristics of aldosterone are reported for three different solvent systems with special regard to its separation from cortisone and cortisol.

ACKNOWLEDGEMENTS

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Uppsala 1956. Almqvist & Wiksells Boktryckeri AB

The surface fine structure of conifer cell walls

By A. ÅKE SVENSSON

With 10 figures in the text

Introduction

From a chemical and technical point of view the cell wall organization of conifer tracheids is of great interest. This is evident when one considers the effect of the cell morphology on the progress of the pulping process and the influence of the surface structure on the papermaking properties of the fibers. Also the ultimate reason for such a typical property as "balloon-swelling" must be the specific organization of the different layers of the cell wall.

Various methods have been used to study the organization of the cell walls. Optical microscopy, electron microscopy and X-ray diffraction have mainly been employed and the contradictory results sometimes obtained can often be referred to the various methods used.

The optical investigations by Kerr and Bailey (5) and Bailey and Vestal (1) indicated a three-layered organization of the secondary wall with the same micellar organization in the outer and inner layer and a different orientation in the middle part of the fiber. This view was later supported by the optical polarization work by Wardrop and Preston (10). Because of the thinness of the primary wall no evidence of its organization could be obtained by optical or X-ray methods and only the electron microscope could be expected to give some information. Hodge and Wardrop (4) by disintegrating delignified mature tracheids in a Waring blender obtained fragments with a woven structure which were considered to be pieces of the primary wall. When the cell walls had been disintegrated no conclusive proof of their organization could be obtained. It should, however, be possible to obtain information of that type by a suitable replica method. Another advantage of such a method would be that it could be expected to unveil the possible influence of chemical and mechanical treatment on the fibers. With this in mind the following investigation of the surface structure of tracheid cell walls was undertaken.

Method

Among the replica methods in use at the time this investigation was started neither one-stage nor two-stage types were quite satisfactory, mainly because of the low resolution of the fiber replicas and the high fall-out percentage during their production. Therefore a pre-shadowed replica method was used. Williams and Wyckoff (11)



Fig. 1. Discharge tube for production of hydrocarbon polymerization films.

applied such a method for investigating protein particles which were shadowed with a heavy metal and thereafter coated with a supporting collodion film. The metal layer was stripped off from the substrate by tearing away the supporting film. Because of the impossibility of stripping off the heavy metal layer from cellulose fibers due to the roughness of their surface, the pre-shadowing method had to be modified in our case. This was done in the following way.

Single fibers were fastened onto small circular pieces of Scotch tape and shadowed with palladium. In order to apply to the fibers a supporting membrane, which should be insoluble in cellulose solvents, the method of König and Helwig (6) for the production of hydrocarbon polymerization films was used. Their apparatus was modified in such a way that the discharge chamber was made in the form of a glass cylinder containing two flat circular aluminium electrodes fastened in two ground glass joints closing the cylinder (Fig. 1). Further, the cylinder had two sidetubes, one for the inlet of the benzene vapour via a needle valve and one leading to an evacuating pump. The electrodes were connected to a 2000 V variable rectifier. The fibers on their tape supports were placed in a flat brass holder on the aluminium anode and were covered with a film a few hundred Å in thickness by allowing the discharge to glow for a few minutes at 1000 V and 0.1 mA at a benzene pressure of 0.03 mm Hg. One by one the fibers were then carefully detached from the tape and placed on electron microscope grids which had previously been covered with the thinnest possible hydrocarbon polymerization film. When the grid was submerged in a cupriethylenediamine solution the fiber floated on the surface of the solution. As viewed through a stereomicroscope, the fiber started to dissolve, leaving the supporting film and its attached heavy metal shadow on the surface of the solution. When, after a few minutes, the fiber was completely dissolved, the grid holding the membrane was removed from the cupriethylenediamine solution and carefully washed twice with distilled water. This latter process was carried out under the stereomicroscope. After the second wash the replica was left on the grid and after it had been dried it could be investigated in the electron microscope.

Due to the membrane covering the grid the resolution of the replicas in electron micrographs was somewhat less than in electron micrographs of dispersed material but still in the region < 100 Å.

Material

All fibers were of Swedish spruce, *Picea abies*, but pulped in different ways. Before taking any replicas the samples were extracted by refluxing in a Soxhlet apparatus first in a mixture of alcohol-benzene in the proportion 1:1 and then in absolute alcohol.

For investigating the carbohydrate middle lamella and the primary wall holo-cellulose fibers manufactured by the sodium chlorite method were used. The wood in the form of chips was treated for two days at 50–60°C in a solution of sodium chlorite containing chlorine to an amount of 60 % of the wood. The solution was changed once. Thereafter 10 % more chlorine was added and the solution left till the chlorine was consumed.

One part of the fibers was investigated as such, a second part was extracted with a borate buffer at pH 10.0 which dissolved away 5 % of the total weight of the fibers in the form of hemicellulose. A third part was extracted with 2 % sodium hydroxide and underwent a weight loss of 15 %.

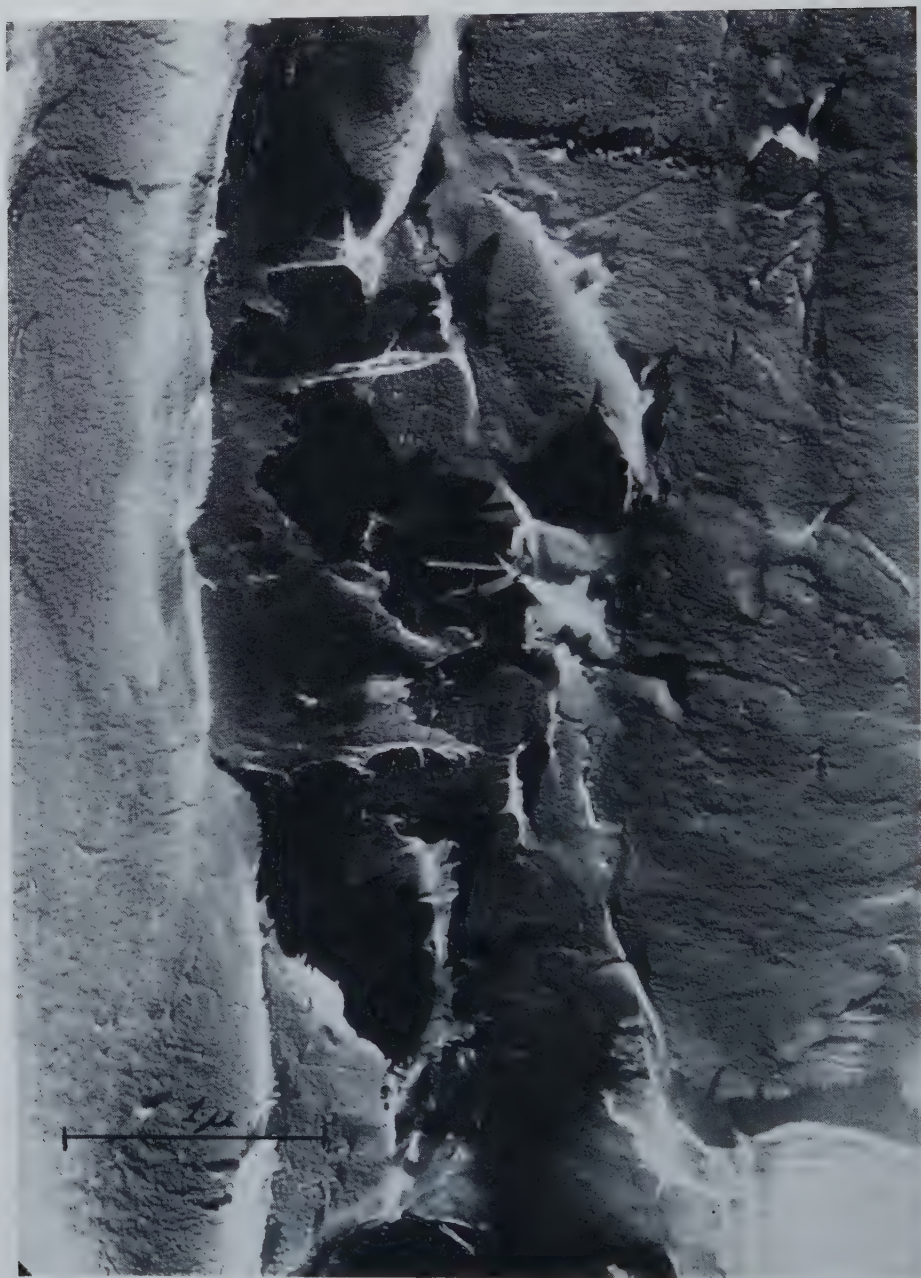


Fig. 2. Surface structure of an untreated hemicellulose fiber.

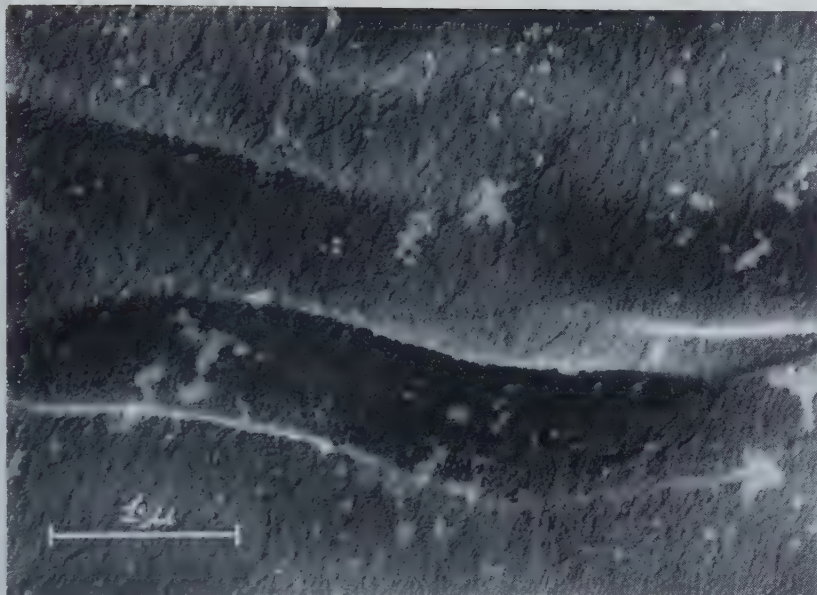


Fig. 3. Surface structure of an untreated hemicellulose fiber with the primary wall appearing.

The secondary wall and the manner in which it could be modified by chemical treatment was investigated on a sulfite pulp and a semichemical pulp. The sulfite pulp which was of a commercial type had an α -cellulose content of 91.0% and a Tappi viscosity of 29.6 cp. Part of it was treated with 18% sodium hydroxide at room temperature. The semichemical pulp had been pulped by calcium bisulfite with 2% free sulphur-dioxide at 125° for ten hours and contained about 15% lignin.

Results

The tracheids delignified according to the holocellulose method contained almost all of the hemicellulose of the original wood and therefore the microfibrils of the cell wall could be expected to be masked. This is actually the case as is shown in Fig. 2. However, the fact that this masking layer of hemicellulose is very thin at some places is revealed by Fig. 3, where the underlying matrix of the primary wall is seen. In this picture the fibrils are, however, incompletely free from the hemicellulose so that only the outer layer of the primary wall appears. The microfibrils of this layer have also a preference for a direction from top right to bottom left in the picture which indicates that within the woven structure of the primary wall very thin ~ 200 Å layers are present which at different levels have different directions. Within each such layer the striation of the fibrils seldom exceeds 30° in the plane of the cell wall.

As shown in Fig. 2 rests from the middle lamella protrude from the primary wall and give it a rough surface. It is probable that these rests are lignin residues from the middle lamella since, as can be shown in electron micrographs of cross-sections of tracheids (9) the carbohydrate content of which has been dissolved away, the remaining middle lamella has a similar irregular boundary to the primary wall. It could be

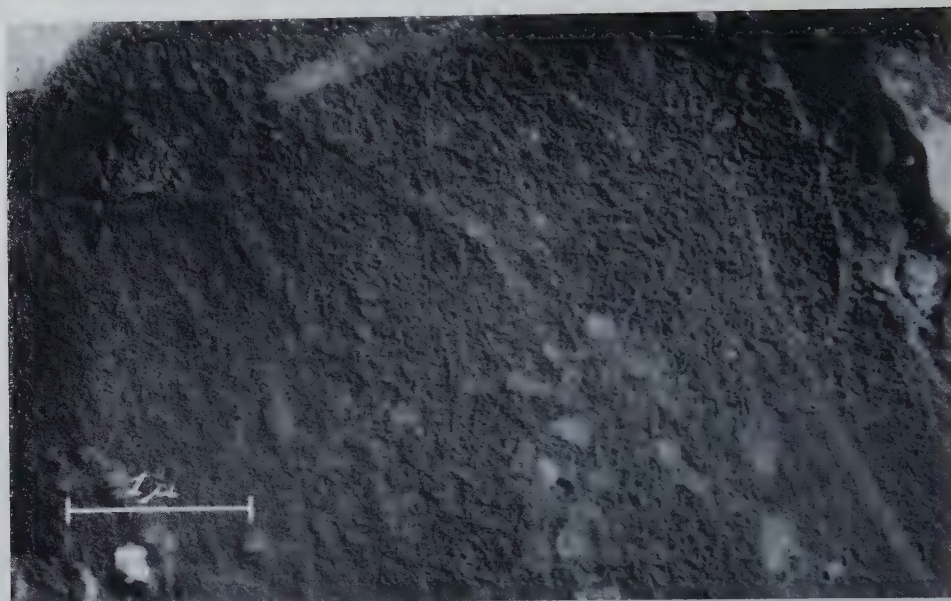


Fig. 4. Surface structure of a hemicellulose fiber, where 5 % of the total weight has been dissolved away in the form of hemicellulose.

argued that the humps protruding from the surface are artefacts from the preparation of the replicas. This cannot be the case, however, since due to the replica method with shadowing of the fibers as a first step, every elevation of the cell wall surface causes a shadow.

In dissolving away part of the hemicellulose at pH 10.0 the surface of the primary wall appears in Fig. 4 as a densely packed woven structure, but with part of the surface still covered with a hemicellulose sheet. This shows that various parts of the surface have different resistance to alkali.

By treatment with 2.0 per cent KOH most of the hemicellulose was dissolved, thus completely unveiling the primary wall. In Fig. 5 the structure found by Frey-Wyssling, Mühlethaler and Wyckoff (3) in cambial walls is shown in a mature tracheid. It can be considered as certain that the whole holocellulose fiber is covered with such a coherent primary wall layer since there was no indication in any of the replicas of parallel alignment of fibrils. The fact that the primary wall is often absent from pulp fibers must be due to the mechanical treatment of the pulp which tears away the primary wall from the secondary wall during the pulping process. In Fig. 5 the previously mentioned thin-layered substructure is clearly seen with the top layer horizontally oriented. The dimension of the microfibrils is of the order of 100 Å but never reaches the region 200 Å. This dimension may be considered to be very reliable since the holocellulose fibers have been delignified with the mildest possible method and not been exposed to any mechanical or chemical treatment that could have disturbed their organization or influenced their dimensions.

The replica technique used gives a good picture of the outer layer of the secondary wall of the sulfite fiber. In Fig. 6 where the longitudinal axis of the fiber is vertical,



Fig. 5. Primary wall of a tracheid cell.



Fig. 6. Outer part of the secondary wall of a tracheid cell with the longitudinal axis vertical.

the parallel alignment of the microfibrils is clearly seen and only few single fibrils happen to cross this direction. Furthermore, the fibrils run in a direction of about 55° to the longitudinal axis. This direction cannot be taken as characteristic for the outer wall, however: as Fig. 7 shows, even an angle of up to 80° may occur. These two values are extremes and several pictures have been obtained with fibril directions in between these two.

In order to be able to measure the above-mentioned inclination of the fibrils relative

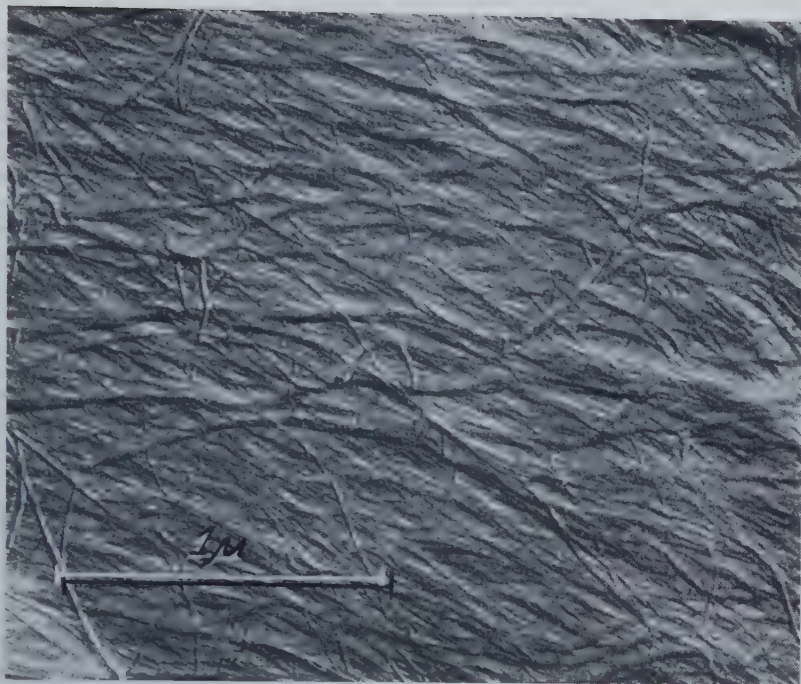


Fig. 7. Outer part of the secondary wall of a tracheid cell showing the greater inclination of the microfibrils to the longitudinal axis as compared with Fig. 6.

to the longitudinal axis, the direction of the latter had to be determined on the photographic plate. This could be easily done since only the replica of one fiber, the border lines of which were visible in the electron microscope, was investigated at a time. Since the border lines were parallel to the longitudinal axis, the direction of the latter could be determined on the electron micrograph.

From Figs. 6 and 7 it can also be inferred that in the outer layer of the secondary wall there is a certain striation of the fibrils within the layer which may be referred both to the original striation in the plant cell wall and to the treatment during the pulping process. The single fibrils extend over long distances, which indicates that there is no striation in a plane perpendicular to the cell wall. Thus the microfibrils run concentrically round the lumen.

One interesting question is what conclusions regarding the orientation of the middle secondary wall can be drawn from the direction of the outer secondary wall. Wardrop and Preston (10) measured the birefringence of the outer and the middle layer in tracheid sections cut at different angles to the longitudinal axis and could therefrom deduce that the orientation of the microfibrils should differ by about 40° in the two layers. According to the measurements reported in this paper the inclination of the microfibrils in the outer secondary wall is between 50 and 80 degrees to the longitudinal axis, which gives an orientation of 10 to 40 degrees in the middle layer. This large variation between different fibers in the orientation of the microfibrils from one fiber to another in the same layer is easily explained by the results of Preston

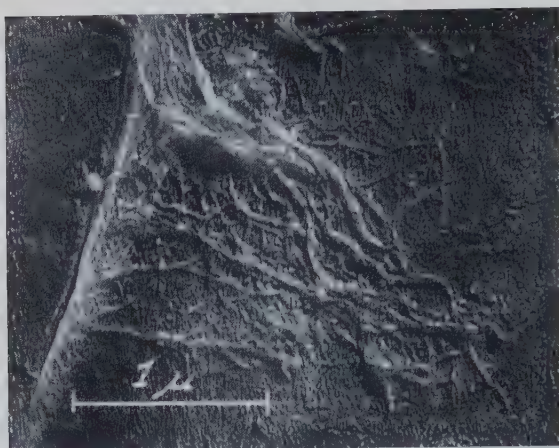


Fig. 8. Rests of the primary wall on the surface of a commercially pulped fiber.

and Wardrop (7) who showed that the inclination of the micells to the longitudinal axis decreased with the number of the growth ring. Thus in our pictures the tracheid of Fig. 6 should correspond to a younger part of the tree than the one of Fig. 7.

Several attempts have been made to determine the sign of the cellulose helix in different parts of the cell wall. From optical investigations by Roelofsens (8) on flax-, ramie- and hemp-fibers it could be deduced that the outer layer of the secondary wall had a Z-helix and the middle layer an S-helix. However, no reliable observations are available on the absolute organization of the different layers in spruce tracheids. From the birefringence measurements mentioned above (10) it could, however, be concluded that the helices of the middle and the outer lamella have the same sign.

With the replica technique used in this investigation it was possible to determine the absolute sign of the helix of the outer secondary wall. This was inferred from the following observations during the dissolution of the fiber. When the fiber and its attached heavy metal and hydrocarbon-polymerization layer on the electron microscope grid was submerged in the cupriethylenediamine solution, the fiber started to dissolve at the surface which came first in contact with the solution. This caused the replica to be flattened out on the liquid of the replica with its outer surface turned up. Thus in this position the replica and the fiber showed the same sign of the helix. However, when the replica was put into the specimen holder on the microscope grid, it was turned upside down which then resulted in a reflected image of it on the photographic plate. As shown in Figs. 6 and 7 the pictures give an S-helix which according to the above analysis should then correspond to a Z-helix of the outer layer of the secondary wall of the fiber. As to whether this is also true of species other than *Picea abies* is uncertain but it should be pointed out that Roelofsens also found the same Z-helix for flax, ramie and hemp.

Very few residues of the primary wall were found in the commercially pulped fibers. As seen in Fig. 8 there are very few rests of the primary wall and it is probable that most of the primary wall had been torn away during the pulping process. This was also indicated by the fact that the characteristic woven structure of it was spoiled. This is contradictory to the results of Emerton and Watts (2) obtained by light microscopy. They claim that large areas of bleached sulfite fibers of the same type as used in this investigation were still covered with the primary wall.

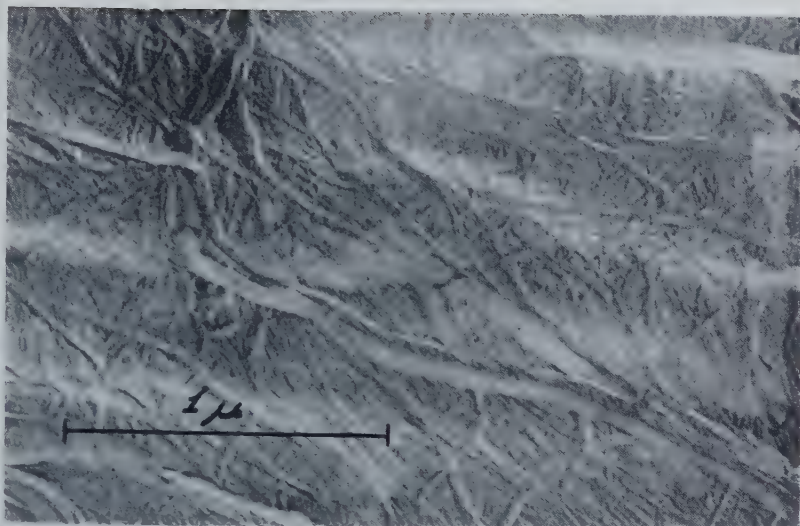


Fig. 9. The outer secondary wall of a tracheid cell treated with 18 % NaOH.

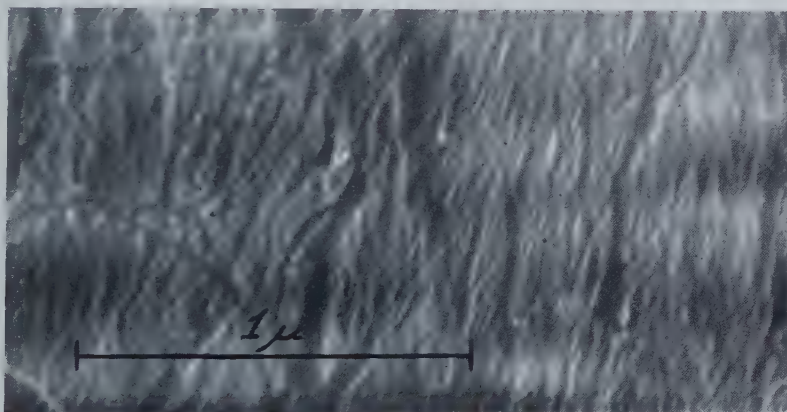


Fig. 10. The outer secondary wall of a semichemically pulped fiber.

The influence of chemical treatment on a fiber tracheid could not be expected to give an appearance of the fiber surface very different from an untreated one since the reaction during a chemical treatment must occur mostly on the molecular level and only to a small degree on the submicroscopic level. However, the fact that very strong chemical treatment may cause changes on the fiber surface is clearly shown by Fig. 9 where the fiber had been treated with cold alkali. This picture gives quite a different impression than Fig. 7, where the microfibrils were entirely parallel. Considerable disorientation of the fibers is evident. There is thus a less dense packing of the fibrils and a corresponding increase in surface.

The untreated semichemical pulp, Fig. 10, with a lignin content of ~ 15 per cent, had a parallel alignment of the microfibrils and showed no peculiarities in this respect relative the sulfite pulp. No lignin residues were present on the surface of the fibers, which gives the impression that the rest lignin is more evenly distributed through the fiber.

Summary

A modified pre-shadowing replica method has been used for studying the surface fine structure of tracheids of Swedish spruce, *Picea abies*. Holocellulose fibers were found to have a thin hemicellulose layer over the coherent woven microfibril structure of the primary wall and the breadth of the microfibrils was found to be about 100 Å. The parallel microfibrils of the outer secondary wall had in a Z-helix an inclination of between 50 and 80 degrees to the longitudinal axis of the fiber. Only residues of the primary wall were found on the surface of commercially pulped fibers. The influence of alkali treatment on the outer secondary wall was studied.

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Über Einstellung des Fehlstellengleichgewichtes in Alkalihalogeniden

Von ERICH SPICAR

Mit 2 Figuren im Text

Einleitung

Jedem, der die Leitfähigkeit von Alkalihalogeniden in Abhängigkeit von der Temperatur untersucht, wird bekannt sein, dass bei Temperaturänderungen, z.B. beim Aufheizen der Kristallprobe, sich das Fehlstellengleichgewicht und damit die elektrische Leitfähigkeit praktisch ohne Verzögerung mit der Temperatur ändert. Dieser experimentelle Befund steht im Widerspruch mit der ursprünglichen Fehlstellentheorie von Schottky-Wagner-Jost, die annimmt, dass Gitterfehler (im Falle der Alkalihalogenide vom Schottkyschen Typ) nur an der Oberfläche gebildet werden können. Man müsste dann nämlich einen von der Grösse der Kristalle abhängigen Nachlauf der elektrischen Leitfähigkeit hinter der Temperatur beobachten (Jost (8)). Dies ist nicht der Fall.

Daraus ist zu entnehmen, dass das Schottkysche Fehlstellenmodell, so richtig es auch in seinen grossen Zügen zweifellos ist, in Details nicht mit der Natur übereinstimmt. Eine Erklärungsmöglichkeit dieser Diskrepanz ergab sich erst in den letzten Jahren durch Annahme von a) inneren Quellen und Senken für Gitterfehler, b) Bildung von schnell diffundierenden elektroneutralen Lückenpaaren.

Wir wollen uns in diesem Artikel vorwiegend mit der zweiten Möglichkeit der schnellen Anpassung an ein neues thermodynamisches Gleichgewicht befassen. Der Vollständigkeit halber sei jedoch auch die erste Möglichkeit kurz diskutiert¹:

Das plastische Verhalten von Kristallen ist, soweit wir bisher wissen, nur durch das Versetzungsmodell zu erklären. Die beiden Grenzfälle einer allgemeinen Versetzung sind die Stufenversetzung (edge dislocation) und die Schraubenversetzung (screw dislocation).

Beide Typen können Sprünge (jogs) in ihren Versetzungslinien besitzen. Bei Stufenversetzungen kann durch Anlagerung von Atomen, die dem Gitter entnommen werden, der Sprung längs der Versetzungslinie wandern. Der eben geschilderte Vorgang würde in einer Substanz mit Schottky-Fehlordnung der Erzeugung von Gitterlücken entsprechen. Ebenso können durch Abgabe von Atomen aus der eingeschobenen Halbebene der Stufenversetzung an das Gitter überschüssige Gitterlücken gefüllt werden (Vernichtung von Gitterlücken).

Rasche Temperaturänderungen sind mit Temperaturgradienten innerhalb der Kristallprobe und daher mit mechanischen Spannungen verbunden. Diesen versucht der Kristall durch plastisches Fließen nachzugeben, d.h. durch die Bewegung von Versetzungslinien. Jede Versetzung

¹ Eine ausführliche Darstellung der Eigenschaften von Versetzungen geben Cottrell (3), Read (13) und Seeger (15).

ist durch Angabe des sogenannten Burgers-Vektors charakterisiert; wie oben erwähnt, kann sie Sprünge enthalten. Nur in dem speziellen Fall, dass sich der Sprung in der Versetzungslinie in Richtung des Burgers-Vektors bewegt, erfolgt diese Bewegung ohne Erzeugung von Gitterfehlern — Zwischengitterionen oder Lücken — (Seeger (16)). Da die Bewegungsrichtung einer Versetzungslinie weitgehend durch die Art der äusseren Spannungen beeinflusst wird (also vorgegeben ist), wird obige Bedingung für „konservative Bewegung“ nicht immer erfüllt sein.

Neben diesen beiden Mechanismen zur Erzeugung oder Vernichtung von Gitterfehlern lassen sich mit Hilfe des Versetzungsmodelles noch weitere ableiten, die das gleiche leisten.

Die zweite Möglichkeit, die eingangs erwähnte Diskrepanz zwischen ursprünglicher Theorie und dem Experiment zu erklären, ergibt sich durch Annahme von schnell-diffundierenden Lückenpaaren, wie dies von Seitz (17) vorgeschlagen worden ist. In einer späteren Arbeit von Dienes (4) wurde berechnet, dass ein solches Paar in KCl, bestehend aus einer K-Lücke und einer Cl-Lücke in unmittelbarer Nachbarschaft, die erstaunlich kleine Aktivierungsenergie von 0,37 eV für Wanderung besitzen sollte. Seither ist von mehreren Autoren der experimentelle Nachweis von Lückenpaaren versucht worden. Die sorgfältigste dieser Untersuchungen ist die von Aschner (1) an KCl. Das Verfahren läuft auf Vergleich der experimentell gemessenen Diffusionskonstante mit einer aus Leitfähigkeitsmessungen unter Anwendung der Einsteinschen Beziehung berechneten hinaus. Eine Abweichung dieser beiden Zahlenwerte voneinander wurde nicht beobachtet. Die Eindeutigkeit dieses Befundes ist nun in der letzten Zeit durch Untersuchungen von Haven (7) und Lidiard (10) etwas in Frage gestellt worden. Beide Verfasser ermittelten nämlich den sogenannten Korrelationsfaktor, der ein Mass dafür ist, inwieweit zwei zeitlich aufeinander folgende Sprünge ein und desselben beobachteten Atomes voneinander abhängig sind. Dies ist tatsächlich der Fall, man findet z.B., dass in der bekannten Beziehung $D_T = f(n/N) D_V$ für kubisch-flächenzentrierte Gitter der Korrelationsfaktor $f = 0,80$ ist. Die Einstein-Gleichung kann dann ganz allgemein geschrieben werden

$$D_T = f \frac{k T}{z^2 e^2 N} \sigma_T.$$

D_T = gemessener Diffusionskoeffizient eines Tracers.

D_V = Lückendiffusionskoeffizient.

n/N = relative Lückendichte bei der Versuchstemperatur.

σ_T = Teilleitfähigkeit im Teilgitter, dem der Tracer angehört.

N = Zahl der Gitterpunkte der Metallionen im cm^3 .

Für Diffusion des Tracers mit Hilfe von Lücken ist $f = 0,80$ in kubisch-flächenzentrierten Gittern, für Diffusion mit Hilfe von Paaren ist jedoch $f = \infty$. Daraus ist zu ersehen, dass durch Überlagerung der beiden eben genannten Diffusionsmechanismen jeder Wert von f zwischen $0,80 < f < \infty$ eingestellt werden kann, je nachdem, welchen relativen Anteil die Diffusion mit Hilfe von Paaren am gesamten Materialtransport hat. Aschner findet in seiner Arbeit (ohne dies explizit anzugeben) $f = 1,0$. Damit ist aber nach dem bisher Gesagten klar, dass die Gültigkeit der Einsteinschen Beziehung mit $f = 1,0$ kein eindeutiger Beweis gegen die Existenz von Lückenpaaren ist.

Es soll daher im nächsten Abschnitt versucht werden, die Konzentration von Lückenpaaren (und halbdissoziierten Paaren) im thermodynamischen Gleichgewicht für KCl und NaCl unter Verwendung der bisher glaubwürdigsten Energiewerte zu berechnen, sowie, im übernächsten Abschnitt, Einfluss der Lückenpaare auf den makroskopisch zu messenden Tracer-Diffusionskoeffizienten.

Konzentration von Lückenpaaren im thermodynamischen Gleichgewicht in Alkalihalogeniden

In der folgenden Rechnung soll die Konzentration der freien und assoziierten Lücken unter Berücksichtigung der elektrostatischen Wechselwirkung zwischen den freien Lücken ermittelt werden. Diese verhalten sich nicht anders als Ionen in einem flüssigen Elektrolyten. Da die Wechselwirkungsenergie die freie Enthalpie G des Realkristalles erniedrigt, verändern sich dadurch auch die Konzentrationen der freien Lücken verglichen mit den ursprünglichen Werten nach Schottky-Wagner (14).

Symbole:

- z = relative Ladung der Lücken.
- ϵ = statische Dielektrizitätskonstante.
- a = Durchmesser des Ions (hier Loches).
- r_0 = Abstand Anion-Kation.
- N_1^i = Zahl der freien Kationenlücken im Kristallvolumen V .
- N_2^i = Zahl der freien Anionenlücken im Kristallvolumen V .
- M_i = Zahl der Paare der Dissoziationsstufe (i) in V .
- N^+ = Zahl der Ionen der Spezies 1 in V .
- N^- = Zahl der Ionen der Spezies 2 in V .
- $N_1^q = N_1^i + \sum M_i + N^+$ = Zahl der Gitterpunkte der Spezies 1 in V .
- $N_2^q = N_2^i + \sum M_i + N^-$ = Zahl der Gitterpunkte der Spezies 2 in V .

Die Theorie von Debye und Bjerrum (siehe z.B. Fowler-Guggenheim (6)) enthält eine kritische Länge

$$q = \frac{z^2 e^2}{2 \epsilon k T}$$

und es wird verlangt, dass $a \gg q$ ist. Dies erreichte Bjerrum dadurch, dass er die Ionen (hier Gitterlücken) in zwei Gruppen teilte. Wir modifizieren die Überlegungen für die vorliegende Aufgabe.

Je nach ihrer Eigenschaft gehören die Gitterlücken einer der nachstehenden Gruppe an:

- 1) Völlig freie Lücken, d.h. solche, die einen grösseren Abstand als q zur nächsten Lücke haben. Diesen Lücken wird willkürlich der Durchmesser q zugeordnet.
- 2) Ist der Abstand zwischen zwei Lücken kleiner als q , so wird dieses Gebilde als Paar bezeichnet, wobei der Index i die Stufe der Dissoziation (oder Anregung) angibt.

Physikalisch kann man sich die verschiedenen Paartypen wie nachstehend vorstellen: Bei der Dissoziation eines Paares im Abstand von z.B. $3r_0$ nach $4r_0$ verändert sich die Dissoziationsenergie und damit die innere Energie des Kristalles nicht wesentlich. Die Zahl der Realisierungsmöglichkeiten, d.h. die Konfigurationsentropie nimmt jedoch stark zu. Daher werden in einem dynamischen Gleichgewicht, wo die Rekombination der Paare deren Dissoziation gerade aufwiegt, auch alle Zwischenzustände zwischen völlig frei und völlig gebunden mit vergleichbaren Mengen von Lücken besetzt sein.

Für NaCl bei 1000°K ist gemäss der angegebenen Gleichung $q = 5,32 r_0$.

Um die Debye-Bjerrumsche Theorie hier anwenden zu können, wird um jede freie

Lücke eine Sperrkugel mit dem Radius $q/2$ gelegt. (Dadurch können freie Löcher einander nicht näherkommen als q .) Weiterhin legt man um die trägere Lücke in einem Paar (im allgemeinen wird dies die Halogeniden-Lücke sein) eine Kugel mit $R = q$, in der sich die andere Lücke auf verschiedenen Plätzen aufhalten kann. Dadurch erreicht man, dass beim „Zusammenstoss“ eines Paares mit einer freien Lücke zwischen 2 der 3 Partner der Abstand grösser als q ist. Die elektrostatische Wechselwirkung der Paare mit anderen Paaren oder freien Lücken wird vernachlässigt, wogegen die Wechselwirkung der freien Lücken untereinander berücksichtigt wird.

Für die freie Enthalpie G des Realkristalles machen wir nachstehenden Ansatz

$$G_{\text{re}} = G_{\text{id}} + \Delta F^L + \Delta F^M = G_{\text{id}} + (\Delta F_1^L + \Delta F_2^L) + \Delta F^M.$$

Darin bedeuten

ΔF_1^L = freie Energie der (freien) Lücken, wenn diese ungeladen wären.

ΔF_2^L = Veränderung der freien Energie durch Wechselwirkung der (freien) Lücken miteinander im Dielektrikum.

ΔF^M = Veränderung der freien Energie des Kristalles durch die Anwesenheit der Paare.

Allgemein gilt

$$\Delta F = \Delta U - T(\Delta S_{\text{misch}} + \Delta S_{\text{Rest}}).$$

Der Entropiebeitrag ΔS wird aufgespalten in die Mischungsentropie und einen Rest, der hauptsächlich aus der Entropieänderung der einer Lücke benachbarten Oszillatoren besteht. Der Rest wird im allgemeinen viel kleiner sein als ΔS_{misch} und gegen diesen Teil vernachlässigt.

Damit folgt

$$G_{\text{re}} = G_{\text{id}} + \Delta U_1^L + \Delta U_2^L - T(\Delta S_1^L + \Delta S^M)_{\text{misch}} + \Delta F_2^L.$$

Darin bedeuten in der hier vorgelegten Näherung

$$\Delta U_1^L = N_1^l \zeta_1^l + N_2^l \zeta_2^l,$$

$$\Delta U^M = \sum_i M_i \psi_i,$$

$$T(\Delta S_1^L + \Delta S^M)_{\text{misch}} = kT \ln K.$$

ζ_1^l = Energie, die benötigt wird, um ein Kation aus dem ungestörten Gitter zu entfernen und an der Kristalloberfläche abzuladen.

ζ_2^l = Ebenso für ein Anion.

ψ_i = Arbeit, die aufgewendet werden muss, um ein Anion wie oben — und gleichzeitig auch ein Kation der Schale (i) um das genannte Anion — aus dem Gitter zu entfernen (Energie zur Bildung eines Paares des Dissoziationsgrades (i)).

$\psi_i = \zeta_1^l + \zeta_2^l - \varepsilon_i^{\text{diss}}$ ist die Definitionsgleichung für die Dissoziationsenergie $\varepsilon_i^{\text{diss}}$. Da hier nur Paare entgegengesetzten Vorzeichens betrachtet werden, ist immer $\varepsilon_i^{\text{diss}} > 0$.

K = Komplexionenzahl für Unterbringung der Elemente $N_1^l, N_2^l, \sum_i M_i$, wobei der Abstand zwischen freien Lücken untereinander und freien Lücken und Paaren immer grösser als q ist.

Eine jede Sperrkugel mit dem Radius $R = q/2$ bedecke p Kationengitterplätze und gleichzeitig p Anionengitterplätze. Aus Gründen der Elektroneutralität gilt in einem Kristall stöchiometrischer Zusammensetzung $N_1^q = N_2^q = N^q$. Man erhält so die Zahl K' der Unterbringungsmöglichkeiten der Paare und freien Lücken (bisher ohne Berücksichtigung der verschiedenen Anordnungen der Kationenlücke im Paar)

$$K' = \frac{\prod_{\alpha=0}^{\alpha=\sigma} (N^q - \alpha p)}{N_1^l! N_2^l! \prod_{i=0} M_i!}$$

mit

$$\sigma = (N_1^l + N_2^l + \sum_i M_i - 1)$$

(Zwischenrechnungen sollen jeweils unterdrückt werden.)

Es muss noch berücksichtigt werden, auf wieviel verschiedene Weisen die Kationenlücken innerhalb der $(\sum_i M_i)$ -Paare angeordnet werden können; dies ist die Zahl K'' .

Dazu muss man ermitteln, wieviel Plätze s_i gleicher Dissoziationsenergie $\varepsilon_i^{\text{diss}}$ es für das Kationenloch um ein gegebenes Anionenloch gibt, d.h. man umgibt das Anionenloch bei (000) mit Kugelschalen und zählt die Kationenplätze innerhalb einer jeden Schale ab.

Tab. 1.

Schale Nr. i	Mittlerer Abstand Anionen- loch-Kationenloch im Paar	Besetzungszahl s_i	Prototyp für die Anordnung
$i=0$	r_0	6	(100)
1	$r_0 \sqrt{9}$	24	(221)
2	$r_0 \sqrt{9}$	6	(300)
3	$r_0 \sqrt{11}$	24	(311)
4	$r_0 \sqrt{13}$	24	(320)
5	$r_0 \sqrt{21}$	130	(421)
6	$r_0 \sqrt{29}$	194	(520)

Die Koordinaten der möglichen Kationengitterpunkte der letzten Spalte (xyz) sind im Vielfachen von r_0 angegeben. Eine genauere Überlegung zeigt, dass Paare mit der Kationenlücke bei (111) vermutlich nicht stabil sind, sondern sofort in den tiefsten Zustand (100) übergeben werden.

Man findet, dass $K'' = \prod_{i=0} s_i^{M_i}$. (Hier ist M_i der Exponent zu s_i im Unterschied zu den hochgesetzten Indizes.)

Damit folgt die gesuchte Komplexionenzahl K

$$K = \frac{\prod_{\alpha=0}^{\alpha=\sigma} (N^q - \alpha p)}{N_1^l! N_2^l! \prod_{i=0} M_i!} \prod_{i=0} s_i^{M_i}.$$

Darin ist $p = \sum_i s_i$; z. B. für $i = 1, 2, 3$ ist $p = 36$.

Für die Bestimmung der Mischungsentropie wird $\ln K$ benötigt, d. h. neben anderem der Ausdruck

$$\ln \Omega = \sum_{\alpha=0}^{\sigma} \ln (N^{\alpha} - \alpha p).$$

Durch Entwicklung des Logarithmus in eine Reihe und geeignete Zusammenfassung der Glieder erhält man

$$\ln \Omega = (\sigma + 1) \ln N^{\sigma} - \left(\frac{p}{N^{\sigma}} \right) \frac{\sigma^2}{2} - \frac{1}{2} \left(\frac{p}{N^{\sigma}} \right)^2 \frac{\sigma^3}{3} - \dots$$

Das Cauchysche Konvergenzkriterium ist für diese Reihe erfüllt. Auch bei dem sehr hohen Wert $p = 1000$ konvergiert die Reihe so rasch, dass es genügt, mit dem ersten Glied zu rechnen. Damit ist $(\Delta S_1^L + \Delta S^M)_{\text{misch}} = k \ln K$ explizit bekannt.

Für die Änderung ΔF_2^L der freien Energie wegen Wechselwirkung der freien Lücken untereinander folgt nach Fowler-Guggenheim (6)

$$\Delta F_2^L = -\frac{8}{3} \sqrt{2} \frac{(N_1^L)^{3/2} |e|^3 \sqrt{\pi}}{V^{1/2} \varepsilon^{3/2} (kT)^{1/2}} \tau(\beta q)$$

$$x \equiv \beta q = \frac{2 \sqrt{2} \pi |e| \sqrt{N_1^L}}{\sqrt{\varepsilon} V k T} q$$

$$\tau(x) = \frac{3}{x^3} [\ln(1+x) - x + \frac{1}{2} x^2].$$

Damit erhält man den endgültigen Ausdruck für die freie Enthalpie G_{re} des Real-kristalles mit $N_1^L = N_2^L$ und $N^+ = N^-$

$$\begin{aligned} G_{\text{re}} = & G_{\text{id}} - \frac{8}{3} \sqrt{2} \frac{(N_1^L)^{3/2} |e|^3 \sqrt{\pi}}{V^{1/2} \varepsilon^{3/2} (kT)^{1/2}} \tau(x) + N_1^L (\zeta_1^L + \zeta_2^L) + \\ & + \sum_{i=0} M_i \psi_i - kT \{ (\sigma + 1) \ln N^{\sigma} + \sum_{i=0} M_i \ln s_i - \\ & - 2 N_1^L \ln N_1^L + 2 N_1^L - \sum_{i=0} M_i \ln M_i + \sum_{i=0} M_i \}. \end{aligned}$$

Die gesuchten Gleichgewichtskonzentrationen N_1^L , M_i werden bestimmt durch die Bedingung

$$dG = \frac{\partial G}{\partial N_1^L} dN_1^L + \sum_{i=0} \frac{\partial G}{\partial M_i} dM_i = 0$$

unter Beachtung der eventuellen Nebenbedingungen.

Durch Differentiation und Verwendung der Nebenbedingungen erhält man aus letzterer Gleichung ein System von unabhängigen transzendenten Gleichungen, aus dem sich, nach geeigneter Vereinfachung des Systemes, die unbekannten Gleichgewichtskonzentrationen M_j und N_1^L bestimmen lassen. Die beiden Ausdrücke lauten ((j) ist ein bestimmter, aus der Zahl der (i) herausgegriffener Index):

$$\frac{M_j}{N^+} \cong s_j \exp \left\{ -\frac{\psi_j}{kT} \right\} \quad (\text{I})$$

und

$$\frac{N_1^i}{N^+} \cong \exp \left\{ -\frac{1}{2kT} \left[(\zeta_1^i + \zeta_2^i) - \frac{2|e|^2}{\epsilon q} \frac{x}{1+x} \right] \right\} \quad (\text{II})$$

mit der Abkürzung

$$x \equiv \beta q = \frac{2\sqrt{2\pi}|e|\sqrt{N_1^i}}{\sqrt{\epsilon} \sqrt{kT}} q.$$

Mittels der ursprünglichen Schottkyschen Theorie kann man x bei gegebener Temperatur abschätzen und damit Gl. (II) iterieren. Verwendet man im Falle NaCl für $(\zeta_1^i + \zeta_2^i) = 2,02$ eV nach Etzel und Maurer (5), so folgt

$$x_{\max} = 1,68 \cdot 10^6 q.$$

Bisher wurde der Durchmesser der „Sperrkugeln“ q noch weitgehend offen gelassen, da dieser wegen $q = z^2 e^2 / 2\epsilon kT$ selbst Funktion der absoluten Temperatur ist. Bei 1000°K war dieses q in NaCl etwa $5,5 r_0$. Wählt man einen etwas grösseren Wert, z. B. $q = 8 r_0$, so kann man das Korrekturglied im Exponenten von Gl. (II) abschätzen. Dieses verändert den Exponenten um $0,0625$ eV, d. h. höchstens 3 %. Eine solche Abweichung in der Aktivierungsenergie liegt jedoch noch ganz innerhalb der erreichbaren Messgenauigkeit, daher ist eine experimentelle Prüfung der Gleichung (II) bisher nicht möglich.

Da q nur im Nenner neben der Eins auftritt ($x = \beta q$), sieht man also, dass die ganze bisherige Ableitung ziemlich unempfindlich gegen den wahren Wert von q ist.

Die beste Vorstellung von dem Zusammenwirken von Paaren und freien Gitterlücken erhält man, indem man die relative Dichte der Paare und der freien Lücken betrachtet. Diese ist

$$\frac{M_j}{M_0} \cong \frac{s_j}{s_0} \exp \left\{ -\frac{\epsilon_0^{\text{diss}} - \epsilon_j^{\text{diss}}}{kT} \right\}.$$

Abb. 1 zeigt dieses Verhältnis aufgetragen über dem Abstand der beiden Lücken im Paar bei NaCl für 1000°K . ϵ_0^{diss} wurde von Bassani und Fumi (2) zu $0,66$ eV berechnet. Die Werte von ϵ_j^{diss} für höhere Dissoziationsgrade $j > 0$ wurden abgeschätzt mittels der Formel:

$$\epsilon_j^{\text{diss}} \cong \frac{e^2}{\epsilon r_j}.$$

Die beiden genannten Verfasser (2) berechneten ebenfalls die Dissoziationsenergie für „angeregten“ Komplex $(\text{Cd}^{++} + \text{Na}_{\square'})$, wenn die Na-Lücke in der Position (200) und Cd^{++} -Ion in der Position (000) ist und fanden die Dissoziationsenergie bereits bei diesem kleinen Abstand weitgehend Coulombisch. Dieses Resultat berechtigt zur Verwendung von obiger Formel für ϵ_j^{diss} .

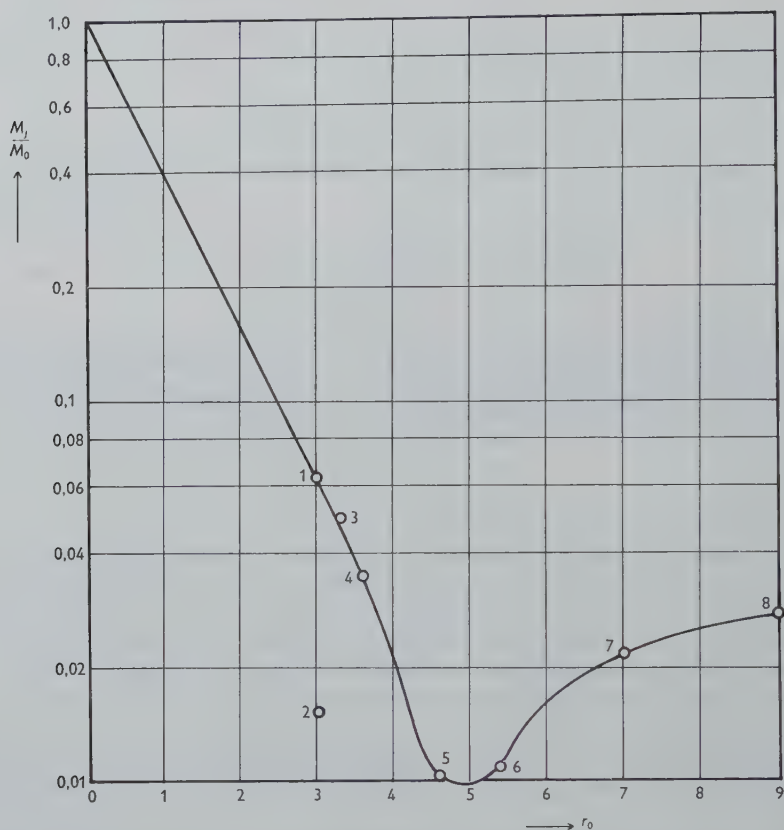


Abb. 1. Relative Dichte von Lückenpaaren in halbdissoziiertem Zustand, bezogen auf die Dichte der Paare im Grundzustand. Die Zahlen an den eingetragenen Punkten geben den Dissoziationsgrad (j) an.

Man beobachtet in Abb. 1 ein ausgeprägtes Minimum bei etwa $5 r_0$. Die Konzentration aller Paare mit $j > 0$ ist um 1–2 Zehnerpotenzen kleiner als die der Paare im Grundzustand ($j = 0$). Daher sieht man auch hier, dass es unwesentlich ist, ab welchem Abstand q man zwei Lücken als frei betrachten will, da die halbdissoziierten Paare keinen merklichen Beitrag zur Gesamtzahl der Lücken und Paare liefern. Die Kurve in Abb. 1 kann auch als eine Art Aufenthaltswahrscheinlichkeit für eine Na-Lücke im Felde einer Cl-Lücke gedeutet werden. Für $r > 5 r_0$ überwiegt der dispergierende Einfluss der Wärmebewegung im Gitter, für $r < 5 r_0$ überwiegt die Coulombische Wechselwirkung und die Na-Lücke wird mit grosser Wahrscheinlichkeit eingefangen. Daher kann man auch den Abstand vom Ursprung bis zum Minimum in r -Richtung als Wirkungsradius der Cl-Lücke bei der herrschenden Temperatur bezeichnen.

Für das Verhältnis der Paare zu den freien Lücken erhält man

$$\frac{M_0}{N_1^i} = s_0 \exp \left\{ \frac{1}{k T} \left[\epsilon_0^{\text{diss}} - \frac{1}{2} (\zeta_1^i + \zeta_2^i) - \frac{e^2}{\epsilon q} \frac{\beta q}{1 + \beta q} \right] \right\}. \quad (\text{III})$$

Unter Verwendung von $\varepsilon_0^{\text{diss}} = 0,66$ eV und $(\zeta_1^l + \zeta_2^l) = 2,02$ eV für NaCl ist der Wert der eckigen Klammer $-0,38$ eV. Damit folgt bei 1000°K für das Verhältnis $M_0/N_1^l = 7,4 \cdot 10^{-2}$. Bei tieferen Temperaturen wird dieser Zahlenwert entsprechend kleiner.

Für KCl erhält man unter Verwendung von $(\zeta_1^l + \zeta_2^l) = 2,08$ eV nach Wagner und Hantelmann (18) und $\varepsilon_0^{\text{diss}} = 0,85$ eV nach Bassani und Fumi (2)

$$\frac{2|e|^2}{\varepsilon q} \frac{x}{1+x} = 0,056 \text{ eV.}$$

Der Wert der eckigen Klammer in Gl. (III) ist dann $(-0,22)$ eV und das Verhältnis M_0/N_1^l am Schmelzpunkt $0,52$. Da der Wert der eckigen Klammer eine Differenz von grösseren, teils berechneten, teils gemessenen Zahlenwerten ist, kann er nicht sehr genau sein und dementsprechend auch nicht das Verhältnis M_0/N_1^l . Wie im Falle des NaCl nimmt auch hier dieses Verhältnis mit fallender Temperatur ab.

Einfluss von Lückenpaaren auf die Tracer-Diffusionskonstante

Wenn der Diffusionsvorgang in einem stöchiometrisch zusammengesetzten und in Bezug auf seine Eigenschaften im thermodynamischen Gleichgewicht befindlichen Alkalihalogenid-Kristall stattfindet und der ganze Materietransport nur durch die Brownsche Bewegung der Gitterlücken geschehen soll, dann ist leicht zu zeigen, dass zwischen dem Diffusionskoeffizienten der Lücken und dem des Tracers die Beziehung $D_T = f(n/N) D_V$ besteht.

Nehmen wir einen Transport durch zwei verschiedene Mechanismen an, so dürfen wir nicht ohne weiteres die Diffusionskoeffizienten beider Mechanismen addieren und daraus eine Aussage über Geschwindigkeit des kombinierten Transportvorganges ableiten. Dagegen ist die Addition der Materieströme physikalisch sinnvoll. Bestehen weiterhin zwischen den Konzentrationen der „Transportmittel“ (in unserem Falle Lücken und Lückenpaare) mathematische Beziehungen, so lässt sich eine physikalisch sinnvolle Gleichung vom Typ $\Sigma j = D \text{ grad } c$ angeben, worin c die Konzentration des Tracers und D der resultierende Diffusionskoeffizient ist. Ein Lückenpaar kann sich bekanntlich durch aufeinanderfolgende Umklappvorgänge durch den Kristall bewegen und damit zur Diffusion beider Komponenten beitragen.

Nachstehend wollen wir nur die praktisch wichtige Diffusion der Alkaliionen in ihrem Teilgitter untersuchen. Dabei nehmen wir an (wie dies auch in der Dienes'schen Arbeit geschehen ist), dass ein benachbartes Na-Ion viel öfter im Zeitmittel in das Lückenpaar hineinspringt als ein benachbartes Cl-Ion (im Falle des NaCl). Anders ausgedrückt bedeutet dies, dass die Chlor-Lücke während einer längeren Zeit $\overline{\Delta t_{\text{Cl}}} = (1/\nu_{\text{Cl}}) e^{+Q_1/kT}$ ein Ruhezentrum ist, um das sich die Na-Lücke im Raum dreht. Zwischen zwei aufeinanderfolgenden Orientierungsänderungen des Paares bei festgehaltener Cl-Lücke vergeht im Mittel die Zeit Δt_{Na} .

Nach obigem gilt also

$$\overline{\Delta t_{\text{Cl}}} \gg \overline{\Delta t_{\text{Na}}} = \frac{1}{\nu_{\text{Na}}} e^{+Q_1/kT}.$$

Q_1 = Aktivierungsenergie für Übergang eines Na-Ions in eine benachbarte freie Na-Lücke.

- A_1 = zugehöriger präexponentieller Faktor.
 Q_3 = Aktivierungsenergie für Übergang eines Na-Ions in die Na-Lücke eines benachbarten Paares.
 ν_{Na} = Frequenz der Gitterschwingungen der Na-Ionen in der Nachbarschaft eines Paares.
 ν_{Cl} = Frequenz der Gitterschwingungen der Cl-Ionen in der Nachbarschaft eines Paares.
 Q_4 = Aktivierungsenergie für Übergang eines Cl-Ions in ein benachbartes Lückenpaar.
 A_4 = zugehöriger präexponentieller Faktor.
 r_0 = Abstand zwischen zwei parallelen Netzebenen ($r_0 = a/2$).
 M_0 = Zahl der Lückenpaare im cm^3 .
 N_1^I = Zahl der freien Lücken im cm^3 .
 N^g = Zahl der Na-Gitterpunkte im cm^3 .

Wir betrachten nun die NaCl Elementarzelle und untersuchen, mit welcher Wahrscheinlichkeit ein radioaktives Na-Ion (der Stern bedeutet die Radioaktivität), das sich ursprünglich in der Position (000) befindet, diese mit Hilfe benachbarter Lückenpaare in Richtung der positiven x -Achse (Diffusionsrichtung) verlassen kann.

Lückenpaare mit ihrer Cl-Lücke bei (100), (010), (001), (010), (001) können zur Diffusion des Na*-Ions beitragen. Die Aufenthaltswahrscheinlichkeit, das Na*-Ion nach der Zeit Δt_{Cl} in einem der zugänglichen Punkte anzutreffen, ist für alle Punkte gleich. Es gilt, aus der Zahl der zugänglichen Na-Gitterpunkte die für Diffusion in (+ x)-Richtung günstigen herauszusuchen. Die Zahl der zugänglichen ist 18, davon sind günstig 5 (4 im Abstand r_0 und 1 im Abstand $2 r_0$ von der ursprünglichen Position bei (000)).

Daher ist die geometrische Wahrscheinlichkeit, das Na*-Ion nach der Zeit Δt_{Cl} in der Ebene r_0 anzutreffen

$$q'_{\text{geom}} = \frac{4}{18} 5 \frac{M_0}{N^g - N_1^I}$$

und es in der Ebene $2 r_0$ anzutreffen

$$q''_{\text{geom}} = \frac{1}{18} 5 \frac{M_0}{N^g - N_1^I}.$$

Man betrachtet nun 5 benachbarte Atomebenen im Abstand von je r_0 . Sie seien mit $p_1[p + (dp/dx)r_0] \dots$ radioaktiven Atomen Na* pro cm^2 besetzt (siehe Abb. 2). Man zählt die Anzahl Atome ab, die während der Zeiteinheit Δt_{Cl} durch die Kontrollfläche (α - α) hindurchtreten. Dies ist die Stromdichte

$$\begin{aligned}
 j &= \left(p - \frac{dp}{dx} r_0\right) q'' - \left(p + \frac{dp}{dx} r_0\right) q' - \left(p + \frac{dp}{dx} r_0\right) q'' + p q' + p q'' - \left(p + 2 \frac{dp}{dx} r_0\right) q'' \\
 &= -r_0 (q' + 4 q'') \frac{dp}{dx}.
 \end{aligned}$$

Die Stromdichte bezogen auf die sec als Zeiteinheit ist

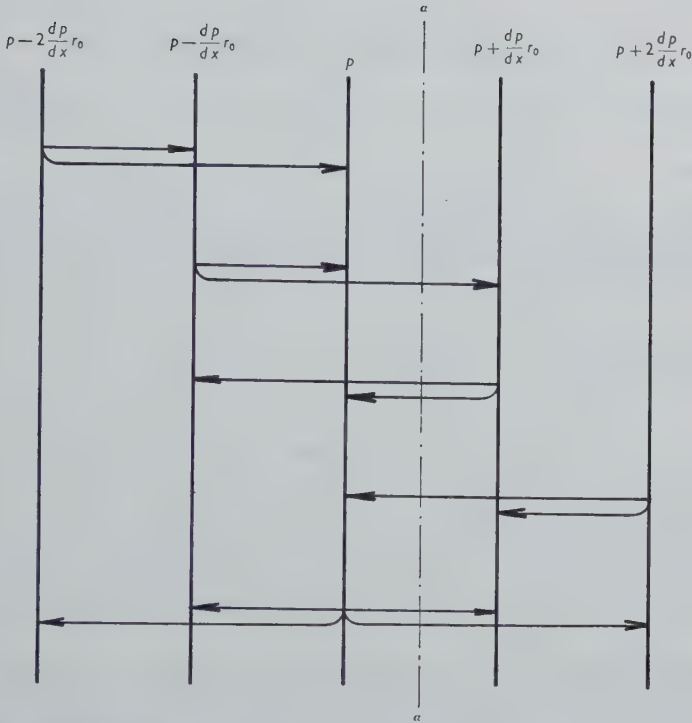


Abb. 2. Benachbarte Netzebenen im Abstand r_0 in $(+x)$ Richtung. Die Pfeile geben die möglichen Übergänge von Na-Ionen beim Transport mittels Lückenpaaren an.

$$J_{\text{Paar}} = \frac{1}{\Delta t_{\text{Cl}}} j = - \frac{r_0}{\Delta t_{\text{Cl}}} (q' + 4 q'') \frac{dp}{dx}.$$

Bezeichnet man mit $c = p/r_0$ die Konzentration des Isotopes pro $[\text{cm}^3]$, so ist

$$J_{\text{Paar}} = - \frac{r_0^2}{\Delta t_{\text{Cl}}} (q' + 4 q'') \frac{dc}{dx}.$$

Für den Diffusionsstrom der Ionen durch Lückentransport findet man ebenso

$$J_{\text{Lücke}} = - r_0^2 \frac{N_1^I}{N^g - M_0} A_1 e^{-\frac{Q_1}{kT}} \frac{dc}{dx}.$$

Diese beiden Gleichungen darf man addieren; der Diffusionskoeffizient für Na-Ionen unter Beteiligung von freien Lücken und Lückenpaaren ist dann

$$D^* \cong r_0^2 \left\{ \frac{N_1^I}{N^g - M_0} A_1 e^{-\frac{Q_1}{kT}} + \frac{25}{18} \frac{M_0}{N^g - N_1^I} A_4 e^{-\frac{Q_4}{kT}} \right\}.$$

Im vorhergehenden Abschnitt wurde die relative Dichte der Lückenpaare $M_0/(N^0 - N_1^I) \sim M_0/N^+ = (M_0/N_1^I) (N_1^I/N^+)$ berechnet. Setzt man diese ein, so folgt

$$D^* = r_0^2 \frac{N_1^I}{N^+} \left\{ A_1 e^{-\frac{Q_1}{kT}} + \frac{25}{18} A_4 s_0 \exp \left[\frac{1}{kT} \left(\varepsilon_0^{\text{diss}} - \frac{1}{2} (\zeta_1^I + \zeta_2^I) - \frac{e^2}{\varepsilon q} \frac{\beta q}{1 + \beta q} - Q_4 \right) \right] \right\}.$$

Der erste Term entspricht dem Beitrag der freien Lücken und der zweite dem Beitrag der Lückenpaare zur phänomenologischen Diffusionskonstante. Die beiden Anteile schätzt man in ihrer Grössenordnung am besten für KCl ab, denn nur für diesen Stoff wurde bisher Q_4 berechnet.

Tab. 2. Zusammenstellung der an KCl gemessenen oder berechneten Energiegrössen in eV.

Name	Q_1 [eV]	$(\zeta_1^I + \zeta_2^I)$ [eV]	$Q_1 + \frac{1}{2} (\zeta_1^I + \zeta_2^I)$
Wagner und Hantelmann (18)	0,78	2,08	
Mott und Littleton (12) . . .		2,08	
Kelting und Witt (9)	0,79–0,94	2,40	
Aschner (1)			1.88

Da Aschners Arbeit mit grosser Sorgfalt durchgeführt worden ist, erscheint der Wert 1,88 eV recht sicher. Zusammen mit den Resultaten von Wagner und Hantelmann sowie Mott und Littleton folgt $Q_1 \cong 0,84 \pm 0,05$ eV. Es ist $Q_4 = 0,38 \pm 0,05$ nach Dienes (4). Die Dissoziationsenergie $\varepsilon_0^{\text{diss}}$ für KCl beträgt nach Bassani und Fumi (2) 0,85 eV. Damit folgt

$$\left(\varepsilon_0^{\text{diss}} - \frac{1}{2} (\zeta_1^I + \zeta_2^I) - \frac{e^2}{\varepsilon q} \frac{\beta q}{1 + \beta q} - Q_4 \right) \cong -0,60 \pm 0,1 \text{ [eV]}.$$

Man erhält so

$$D^* = r_0^2 \frac{N_1^I}{N^+} \left\{ A_1 e^{-\frac{0,84 \text{ [eV]}}{kT}} + \frac{25}{18} A_4 e^{-\frac{0,60 \text{ [eV]}}{kT}} \right\}.$$

Die beiden Exponenten sind von vergleichbarer Grösse; daher kommt es wesentlich auf die Glieder vor den Exponenten an. Diese sind bisher theoretisch nicht bekannt.

Zusammenfassung

1) Es wurde die Konzentration von freien Lücken und Lückenpaaren unter Berücksichtigung der Coulombschen Wechselwirkung zwischen den freien Lücken berechnet, wobei die Entropieänderung, welche die Umgebung einer Lücke durch deren Existenz erfährt, vernachlässigt wurde.

Die relative Konzentration von angeregten Paaren (d.h. solchen mit grösserem Abstand der beiden Lücken als r_0) ist viel kleiner als die von Paaren kleinsten Abstandes und nimmt als Funktion von r stark ab

$$\frac{M_j}{M_0} \cong \frac{s_j}{s_0} \exp \left\{ \frac{\varepsilon_0^{\text{diss}} - \varepsilon_j^{\text{diss}}}{k T} \right\}.$$

Die Konzentration der freien Lücken wurde berechnet zu

$$\frac{N_1^l}{N^+} \cong \exp \left\{ -\frac{1}{2 k T} \left[(\zeta_1^l + \zeta_2^l) - \frac{2 |e|^2}{\varepsilon q} \frac{\beta q}{1 + \beta q} \right] \right\}.$$

Der zweite Term im Exponenten berücksichtigt die elektrostatische Wechselwirkung der freien Lücken. Bei NaCl beträgt die grösstmögliche Änderung der Aktivierungsenergie durch die elektrostatische Wechselwirkung etwa 3 %.

Die relative Konzentration der Lückenpaare verglichen mit den freien Lücken

$$\frac{M_0}{N_1^l} = s_0 \exp \left\{ \frac{1}{k T} \left[\varepsilon_0^{\text{diss}} - \frac{1}{2} (\zeta_1^l + \zeta_2^l) - \frac{e^2}{\varepsilon q} \frac{\zeta q}{1 + \beta q} \right] \right\}$$

hat in NaCl bei 1000°K einen Wert von $7,4 \cdot 10^{-2}$ und nimmt mit fallender Temperatur ab.

Für KCl findet man beim Schmelzpunkt $M_0/N_1^l = 0,52$; auch dieses Verhältnis nimmt mit fallender Temperatur ab.

2) Es wurde der Einfluss von Lückenpaaren auf die Tracer-Diffusionskonstante D_T untersucht

$$D^* = r_0^2 \frac{N_1^l}{N^+} \left\{ A_1 \exp \left(-\frac{Q_1}{k T} \right) + \frac{25}{18} A_4 s_0 \exp \left[\frac{1}{k T} \left(\varepsilon_0^{\text{diss}} - \frac{1}{2} (\zeta_1^l + \zeta_2^l) - \frac{\varepsilon^2}{\varepsilon q} \frac{\beta q}{1 + \beta q} - Q_4 \right) \right] \right\}.$$

Dieser Einfluss ist durch die zweite Exponentialfunktion gegeben. Bei KCl erhält man unter Verwendung der besten bekannten Energiewerte

$$D^* = r_0^2 \frac{N_1^l}{N^+} \left\{ A_1 e^{\frac{0,84 [\text{eV}]}{k T}} + \frac{25}{18} s_0 A_4 e^{-\frac{0,60 [\text{eV}]}{k T}} \right\}.$$

Abschliessend können wir feststellen:

Lückenpaare in Alkalihalogeniden im thermodynamischen Gleichgewicht mit freien Lücken und mit dem Kristall können, wenn überhaupt, nur bei tieferen Temperaturen (trotz ihrer abnehmenden relativen Häufigkeit) die Tracer-Diffusionskonstante beeinflussen. Eine notwendige Bedingung hierfür ist, dass der präexponentielle Faktor $(25/18) s_0 A_4$ den Faktor A_1 überwiegt. Zahlenwerte für A_4 sind bisher noch nicht bekannt geworden. Aus den Experimenten von Aschner (1) und Mapother *et al.* (11) darf geschlossen werden, dass bei KCl, NaCl und NaBr Lückenpaare in keinem, oberhalb des Knickpunktes in der Leitfähigkeitskurve liegendem Temperaturbereich eine grössere Bedeutung haben können.

Da bei raschen Temperaturänderungen und nachfolgenden Änderungen der Konzentration von freien Lücken und Paaren sicher lokales Gleichgewicht zwischen Lücken und Paaren erhalten sein wird und nach Vorstehendem Paare bisher weder

beobachtet werden konnten noch die Berechnung in dieser Arbeit wesentliche Konzentrationen ergab, können Lückenpaare bei Temperaturänderungen nicht für die schnelle Anpassung an das neue thermodynamische Gleichgewicht verantwortlich gemacht werden. Damit verbleibt die Annahme von inneren Quellen und Senken für Gitterlücken die einzige Erklärung für die experimentellen Befunde.

Diese Veröffentlichung ist ein Teil einer grösseren Arbeit, welche von Herrn Docent R. Lindner angeregt wurde.

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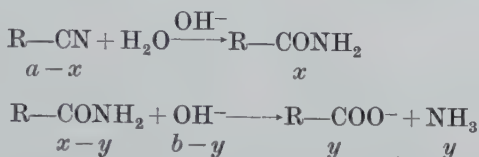
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The alkaline hydrolysis of acetonitrile

By SIGVARD WIDEQVIST

There have been many discussions about the alkaline hydrolysis of nitriles. The reaction may be considered to take place in two consecutive steps, as follows:



In the first step, leading to an amide, the hydroxy ions act only as a catalyst; in the second step the hydroxy ions are consumed and the final products are carboxylic acid anions and ammonia. If the concentration of nitrile is denoted $a-x$, the concentration of alkali $b-y$, the concentration of amide $x-y$, and the concentration of carboxylic acid and ammonia y , we get the following differential equations for the rate of reaction:

$$dx/dt = k_1(a-x)(b-y), \quad (1)$$

$$dy/dt = k_2(x-y)(b-y). \quad (2)$$

The alkaline hydrolysis of acetonitrile and propionitrile was investigated for the first time by Peskoff and Meyer [1]. They found, however, that the reaction followed a single-step second-order kinetics and therefore assumed that the first step was very fast so that the rate of reaction was determined only by the second step. Eq. (2) may also be written in the form

$$dy/dt = k_2(a-y)(b-y) - k_2(a-x)(b-y). \quad (3)$$

On combining with eq. (1) we get

$$dy/dt = k_2(a-y)(b-y) - (k_2/k_1)dx/dt. \quad (4)$$

If $k_1 \gg k_2$, the second term in the right-hand member disappears and we get the expression for a single-step reaction. In spite of that the interpretation of Peskoff and Meyer is erroneous. For the hydrolysis of propionitrile they obtained the rate

constant 0.00888. From eq. (4) it follows that this rate constant should be identical with k_2 , i.e. the rate constant for the alkaline hydrolysis of propionamide. But according to the measurements of Peskoff and Meyer this rate constant is 0.1353. This discrepancy has been noted by Kilpi [2] and he has pointed out that on the basis of their data the velocity of the nitrile hydrolysis has been measured. The nitrile reaction should thus be slower than the amide reaction.

Eq. (4) can also be written

$$(k_1/k_2) dy/dt = k_1(a-y)(b-y) - dx/dt. \quad (5)$$

If $k_2 \gg k_1$, the left-hand member disappears and we get

$$dx/dt = k_1(a-y)(b-y). \quad (6)$$

By division with eq. (1) we get

$$a-x = a-y \quad (7)$$

and thus $dy = dx$. It follows that

$$dy/dt = k_1(a-y)(b-y). \quad (8)$$

Kilpi's interpretation is thus correct.

Some years ago a critical investigation on the alkaline hydrolysis of propionitrile was made by Rabinovitch and Winkler [3]. They state that the hydrolysis proceeds through the amide to yield the corresponding acid and ammonia. Curiously enough they also state that at all alkali concentrations considered, analysis must be made for total amide *and* ammonia to determine the velocity of the nitrile hydrolysis. It should not be sufficient to determine the ammonia alone. That this opinion is not correct is easily seen from the following.

Consider the equation system (1), (2). By applying the method of changing the time variable (Wideqvist [4]) the reaction order can be reduced. On putting $(b-y)dt = d\theta$ we thus get

$$dx/d\theta = k_1(a-x), \quad (9)$$

$$dy/d\theta = k_2(x-y). \quad (10)$$

On integrating we get

$$x = a(1 - e^{-k_1\theta}) \quad (11)$$

and

$$y = a \left[1 + \frac{k_2}{k_1 - k_2} e^{-k_1\theta} - \frac{k_1}{k_1 - k_2} e^{-k_2\theta} \right] \quad (12)$$

where $\theta = \int_0^t (b-y) dt$.

Now consider the function

$$y = f(\theta). \quad (13)$$

The area between the curve and the θ -axis is

$$A = \int_0^{\theta} f(\theta) d\theta = \int_0^{\theta} y d\theta. \quad (14)$$

Combining eq. (12) and (14) we get

$$A = a \int_0^{\theta} \left[1 + \frac{k_2}{k_1 - k_2} e^{-k_1 \theta} - \frac{k_1}{k_1 - k_2} e^{-k_2 \theta} \right] d\theta \quad (15)$$

and on integrating

$$A = a \left[\theta - \frac{k_2}{k_1 (k_1 - k_2)} e^{-k_1 \theta} + \frac{k_1}{k_2 (k_1 - k_2)} e^{-k_2 \theta} - \frac{k_1 + k_2}{k_1 k_2} \right]. \quad (16)$$

On eliminating $e^{-k_1 \theta}$ between eq. (12) and (16) we get

$$k_1 = \frac{y}{a\theta - A - \frac{a}{k_2} (1 - e^{-k_2 \theta})}. \quad (17)$$

From eq. (17) it follows that the rate constant k_1 can be calculated from the concentration of ammonia alone. The use of eq. (17) makes the knowledge of the rate constant k_2 necessary. The determination of k_2 presents no difficulty as the intermediate amides are usually easily prepared.

Some new aspects of the reaction can be obtained on eliminating $e^{-k_2 \theta}$ from eq. (17): Consider the function

$$A = F(\theta). \quad (18)$$

The area between the curve and the θ -axis is

$$B = \int_0^{\theta} F(\theta) d\theta = \int_0^{\theta} A d\theta. \quad (19)$$

But according to eq. (17) we have

$$A = a\theta - (a/k_2)(1 - e^{-k_2 \theta}) - y/k_1. \quad (20)$$

From eq. (14) and (19) we get on integrating

$$B = a\theta^2/2 - a\theta/k_2 - A/k_1 + (a/k_2^2)(1 - e^{-k_2 \theta}). \quad (21)$$

On eliminating $e^{-k_2\theta}$ between eq. (20) and (21) we get

$$y = k_1 k_2 (a\theta^2/2 - B) - (k_1 + k_2) A. \quad (22)$$

From eq. (22) the product $k_1 k_2$ and the sum $(k_1 + k_2)$ can be calculated, and the rate constants are thus the roots of the equation

$$k^2 - pk + q = 0, \quad (23)$$

if $p = (k_1 + k_2)$ and $q = k_1 k_2$. It is thus impossible to distinguish between k_1 and k_2 , if neither of them is known before. This implies that an interchange of the rate constants has no influence upon the rate of reaction in the second reaction step. This is also seen from the symmetrical form of eq. (12).

The possibility of interchanging the rate constants without alterations in the variable y affords a new method for calculating k_1 . First k_2 is determined by measuring the rate of the amide hydrolysis. We then consider the equation system

$$dz/dt = k_2 (a - z) (b - y), \quad (24)$$

$$dy/dt = k_1 (z - y) (b - y). \quad (25)$$

Here the variable z is referred to a hypothetical reaction with the rate constant k_2 for the first step and k_1 for the second step. Division of eq. (25) with $(a - y)(b - y)$ gives

$$\frac{dy}{(a - y)(b - y)} = k_1 \frac{z - y}{a - y} dt = k_1 \left(1 - \frac{a - z}{a - y} \right) dt. \quad (26)$$

On integration we obtain

$$\ln \frac{a(b - y)}{b(a - y)} = (b - a) k_1 \left(t - \int_0^t \frac{a - z}{a - y} dt \right). \quad (27)$$

The quantity $(a - z)$ is easily calculated from eq. (24). On putting $(b - y) dt = d\theta$ we get

$$dz/d\theta = k_2 (a - z) \quad (28)$$

and on integrating

$$\log (a - z) = \log a - 0.4343 k_2 \theta, \quad (29)$$

where $\theta = \int_0^t (b - y) dt$. It is thus possible to evaluate the integral $\int_0^t [(a - z)/(a - y)] dt$ by graphical or numerical methods. The rate constant k_1 is then easily calculated from eq. (27).

Experimental

The theoretical results obtained above were tested against the data for the alkaline hydrolysis of acetonitrile. The measurements were performed at $25.0 \pm 0.02^\circ \text{C}$. The reaction was followed by use of the ion exchange method previously described by the present author [5]: Samples were taken with a 5 ml pipette and allowed to flow through a cation exchanger containing Amberlite IR-120 and titrated with standardized sodium hydroxide. In this way the amount of acetic acid, y , produced during the reaction was determined. The alkali used for the hydrolysis of the nitrile was sodium hydroxide.

The rate constant k_1 for the nitrile hydrolysis was calculated in two ways, namely from eq. (17) and from eq. (27). Application of eq. (27) seemed to be the best method. The rate constant k_2 for the amide hydrolysis has previously been determined by Wideqvist [5] and by Peskoff and Meyer [1], and the mean value 0.1343 was used for the calculations.

The integrals $\theta = \int_0^t (b-y) dt$ and $A = \int_0^t y d\theta$ were evaluated by the use of the trapezoid formula and the integral $\int_0^t [(a-z)/(a-y)] dt$ by means of Simpson's formula. The experimental data and the results of the calculations are shown in Tables 1 and 2, where t is the time in hours, S denotes the integral $\int_0^t [(a-z)/(a-y)] dt$, L the expression $\log \frac{a(b-y)}{b(a-y)}$, and E the expression $(a/k_2)e^{-k_2\theta}$. The mean values of k_1 are calculated by the method of least squares, and they show good agreement. From eq. (17) we get $k_1 = 0.00717$ and from eq. (27) 0.00716.

Table. 1. The hydrolysis of acetonitrile by alkali.

The calculation of k_1 from eq. (17). $a = 0.20380$; $b = 0.25027$.

t	$y \times 10^5$	$b-y$	θ	A	E	$a\theta$	$k_1 \times 10^3$
0	0	0.25027	0	0	1.5175	0	—
4	12	.25015	1.001	0.00006	1.3266	0.2040	—
8	27	.25000	2.001	.00026	1.1599	0.4078	—
24	275	.24752	5.981	.00627	0.6796	1.2190	7.34
48	852	.24175	11.853	.03938	.3089	2.4156	7.30
72	1525	.23502	17.574	.1074	.1433	3.5815	7.26
96	2203	.22824	23.133	.2110	.0679	4.7145	7.21
120	2860	.22167	28.532	.3477	.0329	5.8189	7.17
144	3501	.21526	33.775	.5144	.0164	6.8833	7.19
168	4103	.20924	38.869	.7081	.0082	7.9215	7.19
192	4672	.20355	43.822	.9254	.0042	8.9310	7.20
216	5190	.19837	48.646	1.1633	.0022	9.9140	7.17
240	5702	.19325	53.345	1.4192	.0012	10.8717	7.19

Table 2. The hydrolysis of acetonitrile by alkali.

The calculation of k_1 from eq. (27). The same data are used as in Table 1. $a = 0.20380$;
 $b = 0.25027$.

t	$a - z$	$a - y$	S	$t - S$	L	$k_1 \times 10^3$
0	0.20380	0.20380	0	0	—	—
4	.17817	.20368	3.750	0.251	—	—
8	.15577	.20353	7.030	0.970	—	—
24	.09127	.20105	16.557	7.443	0.00104	6.93
48	.04148	.19528	24.191	23.81	.00344	7.11
72	.01924	.18855	27.805	44.20	.00641	7.16
96	.009119	.18177	29.559	66.44	.00961	7.15
120	.004416	.17520	30.429	89.57	.01291	7.13
144	.002184	.16879	30.870	113.13	.01634	7.15
168	.001102	.16277	31.099	136.90	.01980	7.17
192	.000567	.15708	31.220	160.78	.02328	7.18
216	.000296	.15190	31.284	184.72	.02664	7.15
240	.000158	.14678	31.320	208.68	.03018	7.16

Summary

The hydrolysis of acetonitrile in aqueous sodium hydroxide at 25° has been studied. The reaction takes place in two steps with acetamide as intermediate product, and the amide is hydrolyzed about 19 times as fast as the nitrile. The reaction was followed by determining the acetic acid formed during the second step of the reaction. A mathematical analysis of the reaction showed that an interchange of the rate constants for the first and second step had no influence upon the rate of formation of the final products. On this basis a new principle for the calculation of the rate constant for the first step has been suggested.

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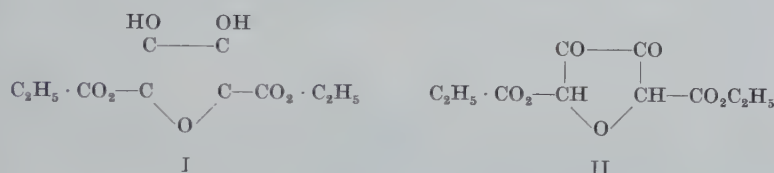
Wirkungen eines Bisreduktions und eines Guanidyl-Chinons auf Kresse-Keimung und Tumor-Entwicklung

Von HANS VON EULER und HANS HASSELQUIST

Mit 2 Figuren im Text

Zur Chemie des Bisreduktions aus Dioxy-furan-dicarbon-säureester

Das dem hier zu besprechenden Bisreduktion zugrundeliegende Furanderivat DFDC wird dargestellt nach JOHNSON und JOHNS¹ bzw. nach HINSBERG² aus Diglykolsäureester, Oxalsäure-diäthylester und Natriumäthylat, deren Mischung nach 3tägigem Stehen bei Zimmertemperatur mit HCl übersättigt wird (Schmpt. 189°).



JOHNSON und JOHNS haben ihr Produkt als 3,4-Dioxy-furan-2,5-dicarbon-säureester (II) formuliert. Hierzu ist anzuführen, dass die Substanz in Lösung mit Phenylhydrazin nicht reagiert, also keine Ketoreaktion zeigt. Über ein Keto-Endiol-Gleichgewicht zwischen I und II ist nichts bekannt. Der Substanz DFDC kommt also die Formel I zu.³ Ihr Spektrum wurde schon früher von H. HASSELQUIST (l.c. S. 123) gemessen; es zeigte ein Absorptions-Maximum bei 284 mμ und log c = 4,25. Eine neue Aufnahme ergab die in Fig. 1 dargestellte Kurve mit einem Maximum bei 282,5 mμ und E_{max} = 4,25 (Konzentration der Lösung 8,15 γ/ml).

Erhitzt man den Dioxy-furan-dicarbon-säure-ester in essigsaurer Lösung 3 Stunden mit Phenylhydrazin, so tritt keine Reaktion ein, der Ester bleibt unverändert; dies zeigt, dass der Ester in Form I vorliegt, Form II würde ein Osazon liefern.

Wenn der Furanring des DFDC aufgespalten wird, was rel. leicht in alkalischer Lösung erfolgt, so verhält sich DFDC gegen Tillmans-Reagens, TR, folgendermassen:

Setzt man zu der wässrigen Suspension von DFDC einige Tropfen TR-Lösung,

¹ T. B. JOHNSON u. C. O. JOHNS, Am. Chem. Journ. 36, 290 (1906).

² O. HINSBERG, Ber. d. dtsh. chem. Gas. 45, 2413 (1912).

³ W. M. HOEHN, Iowa State Coll. J. Sci. 11, 66 (1936). — H. HASSELQUIST, Dieses Arkiv 7, nr. 16 (1955). Der Dioxy-furan-dicarbon-säure-ester zeigt im UV grünliche Fluoreszenz, was ebenfalls auf die Struktur I hindeutet.

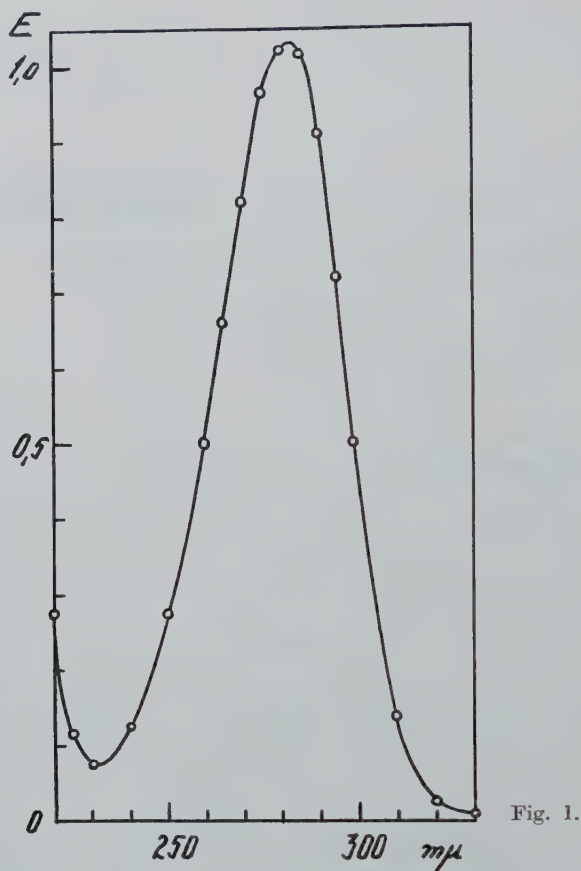


Fig. 1.

so tritt langsam Entfärbung ein, die bei pH 5–6 der Lösung unter erheblichem Verbrauch von TR weiter fortschreitet.

Erwärmt man DFDC in alkalischer Lösung (pH 9) 5 Minuten auf dem kochenden Wasserbad und säuert dann mit Essigsäure an, so werden sogar grössere Mengen von TR sofort entfärbt.

Quantitative Endiol-Titrationen des DFDC (Mol. Gew. 244)

Mit Tillmans-Reagens. 4,8 mg DFDC in 10 ml Wasser suspendiert, mit einer 0,00825-n. TR-Lös. bei etwa 50° titriert, verbrauchten 9,75 ml der TR-Lösung.

$9,75 \times 0,00825 = 0,0804$ mÄquiv. TR entspr. $2 \times 4,8 / 244 = 0,0394$ mÄquiv. DFDC.

Hieraus ergibt sich die Bildung von

$$\frac{0,0804}{0,0394} = 2,04 \text{ Endiol-Gruppen.}$$

Zwei Jodtitrationen der DFDC-Suspensionen in 10 ml Wasser (+KAc):

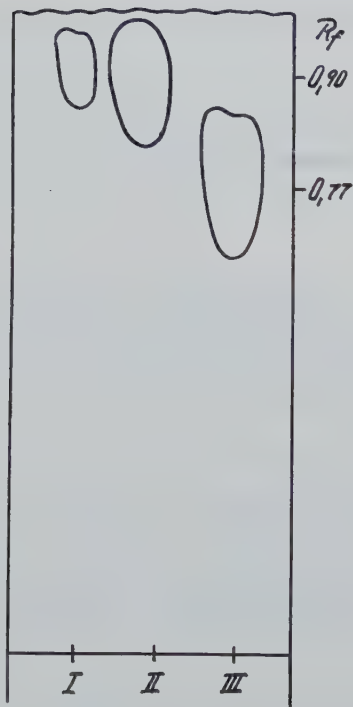


Fig. 2. Flecken I u. II aus DFDC. —
Flecken III Trioseredukton.

a) 4,0 mg = 0,0328 mÄquiv. DFDC verbrauchten 5,4 ml der 0,102 m.
Jodlös. = 0,0552 mÄquiv. Jod. Daraus berechnet sich der Gehalt

1,7 Endiol-Gruppen per Mol DFDC.

b) 3,8 mg = 0,0287 mÄquiv. DFDC verbrauchten 7,3 ml der 0,00708 m.
Jodlös. = 0,0517 mÄquiv. Jod. Daraus berechnet sich der Gehalt

1,8 Endiol-Gruppen per Mol DFDC.

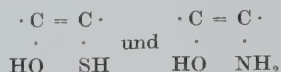
Der mittlere Endiol-Gehalt wird also durch die Jodtitrationen etwas geringer gefunden (1,75) als durch die TR Titration, schliesst sich aber dem mit TR erhaltenen Ergebnis genügend an, um den Schluss zu gestatten, dass zwei Endiolgruppen im Molekül vorliegen.

Papierchromatographie

Munktell OB. Mischung: 4 Tle Butanol + 1 Tl Eisessig + 1 Tl Wasser. Bei der Entwicklung mit 0,005-n. TR-Lösung in 50%igem Alkohol bildet sich auf dem noch feuchten (essigsäuren) Papier (um aci-Redukton nachzuweisen) im Laufe der Chromatographierung langsam ein wenig Endiol. Dagegen wurden bei Verwendung der alkalisch behandelten Lösung Flecken erhalten, die in allen Teilen TR sofort entfärbten und rascher wanderten als die des Triose-Reduktone (siehe Fig. 2).

Als Produkt der Alkali-Behandlung des Dioxy-furan-dicarbonsäureester erhalten wir also ein Bis-redukton mit konjugierten Endiolgruppen; es dürfte das erste bisher nachgewiesene Bis-endiol darstellen.

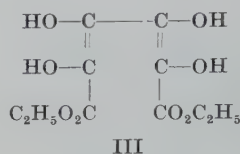
Über Bis-reduktone mit konjugierten Gruppen



wird demnächst an anderer Stelle berichtet.

Salze

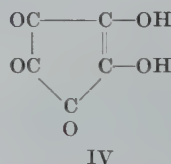
Der Dioxy-furan-dicarbonsäure-ester liefert direkt ein farbloses Na-Salz, das aus der wässrigen Lösung mit Alkohol ausgefällt werden kann. Die Lösung dieses Salzes entfärbt TR nicht schneller als der Ester selbst, sie enthält also den Furanring unverändert.



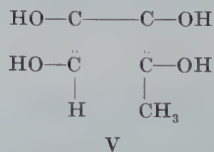
Durch Oxydation ist die Bildung einer noch unbekannten Tetra-keto-hexonsäure zu erwarten.

200 mg Furandicarbonsäure-ester + 2 g KAc in 50 ml Wasser werden mit 0,1-n. Jodlösung (Stärke als Indikator) bis zum Umschlag versetzt. Nach Abschluss der Oxydation bleibt die Lösung nach Zugabe von 0,53 g Phenylhydrazin. HCl + KAc + 1 ml Eisessig 18 Stunden bei 20° stehen. Die gelbrote krystallinische Fällung wird abfiltriert, gewaschen und getrocknet. Ausbeute 70 mg vom Schmp. 130–132°.

Krokonsäure, welcher meist die nebenstehende Formel IV zugeschrieben wird¹ könnte durch geeignete Reduktion das Bis-endiol eines Keto-cyclo-pentadiens liefern.



Andere Bis-reduktone haben wir aus Monosen zu gewinnen versucht. Vor etwa 8 Jahren fanden wir², dass nach Behandlung von D-Xylose in 65° warmer alkalischer Lösung bei der Titration mit TR-Lösung „so viel TR verbraucht wird, wie wenn aus einem Mol der Pentose zwei Endiol-Gruppen gebildet würden. Dieser Vorgang tritt vielleicht zunächst ohne Spaltung des Pentosemoleküls ein, etwa unter Bildung eines Bis-endiols



welches dann bei der Oxydation durch TR zerfällt“.

Bei der alkalischen Hexose-Spaltung tritt eine Vorstufe des Triose-Reduktions auf³, die sich aber nicht als Hexose-bis-Reduktion erwies.

¹ Siehe aber G. CARPÉNI, Journ. Chim. physique 35, 233 (1938).

² EULER u. H. HASSELQUIST, Karrer-Festschrift, Experientia 5, 81 (1949).

³ EULER u. HASSELQUIST, Lieb. Ann. 588, 205 (1954).

Keimungsversuche an Krasse (*Lepidium sativum*) mit DFDC (501)

Samen von Krasse 4 Stunden in Wasser, dann in Lösung von 10–40 mg Sbst. 501 (Dioxy-furan-dicarbonsäure-ester) bei 20° und pH 6,2 gequollen, dann mit der gleichen Lösung in Schalen zwischen Filtrierpapier zum Keimen gebracht.

Starke Verzögerung der Keimung gegenüber der Wasserkontrolle. Nach etwa 40 Stunden werden die Keimlinge sichtbar; die Filtrierpapierdecken werden abgenommen und die Samen dem diffusen Tageslicht ausgesetzt.

Nach 5 Tagen mittlere Längen in mm:

Konzentration der Lösung	Mit 501 behandelt		Wasserkontrolle	
	Wurzeln	Stengel	Wurzeln	Stengel
0,04 %	1–3	6	30	25
0,01 %	8–15	16		

Die mit 0,04 % DFDC behandelten Pflänzchen können wegen der Kürze des Wurzelansatzes nicht aufrecht stehen, die Stengel (Sprossachsen) sind dicker als die normalen und stark gekrümmt. Blätter normal.

Was die Art dieser Keimungshemmung betrifft, so ziehen wir in Betracht, dass die Endiolgruppen auf gewisse, an der Entwicklung beteiligte Enzymsysteme störend einwirken, und zwar durch Entziehung ihrer Aktivatoren oder durch Blockierung ihrer Coenzym-bindenden Stellen.

Guanidyl-p-Chinon (Sbst. 502)

Unter den Stoffen, die sich als Inhibitoren des Tumorwachstums erwiesen haben, sind besonders die Chinone (und die Chinon-methide) bemerkenswert. Die Hemmungswirkungen der Chinone wurden von uns mehrmals erwähnt (Dieses Arkiv 6, nr 34; 6, nr 18; 6, nr 10 u. 12), so dass wir uns darauf beschränken können, auf die Arbeiten von H. LETTRÉ² (Nachweis von Mitosen-Hemmungen), R. KUHN³, E. F. LEHMANN⁶, H. DRUCKREY⁴, O. HOFFMANN-OSTERHOF⁵, besonders aber auf die hochaktiven tumorhemmenden Chinonderivate von DOMAGK und MITARB.⁷ hinzuweisen.

Wie aromatische o-Chinone vom Typus des Adrenochroms scheinen auch p-Chinon-Derivate als Regulatoren von Redox-Vorgängen am tierischen Stoffwechsel wesentlich teilzunehmen. Als Antagonisten fungieren SH-Verbindungen.

Die wirksamsten der von DOMAGK u. Mitarb. synthetisierten und geprüften Substanzen enthalten bekanntlich die auch im Triäthylen-melamin wirksame Methylenimin-Gruppe, z. B. das Chinonderivat

¹ Hinsichtlich der Wirkungen von o-Chinonen vom Typus des Adrenochroms, dessen anti-mitotischen Effekt LETTRÉ betont hat, siehe auch EULER u. S. DI BELLA, Gazzetta Chim. Italiana 82, 647 (1952).

² H. LETTRÉ u. Mitarb., Z. physiol. Chem. 291, 99 (1952). Siehe auch H. S. REED, Experientia 5, 237 (1947).

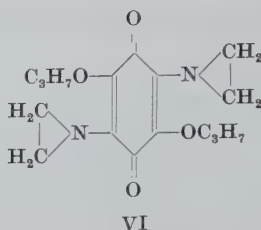
³ R. KUHN u. H. BEINERT, Chem. Ber. 76, 904 (1943); 80, 21 (1947).

⁴ H. DRUCKREY, P. DANNEBERG, D. SCHMAHL, Arzneimittelforsch. 3, 151 (1953).

⁵ O. HOFFMANN-OSTERHOF, Sitz. Ber. Österr. Akad. Wiss. II b, 157, 277 u. 61 (1948).

⁶ E. F. LEHMANN, Experientia 3, 223 (1947).

⁷ G. DOMAGK u. S. PETERSEN, Naturwiss. 41, 10 (1954). — G. DOMAGK, S. PETERSEN u. W. GAUSS, Z. Krebsforsch. 59, 616 (1954).



Wegen der vielfachen biologischen Wirkungen der Guanidylgruppe (z.B. im Streptomycin¹) haben wir ein Guanidyl-chinon in den Kreis unserer Untersuchungen gezogen. Ein hier besprochenes Präparat haben wir folgendermaassen dargestellt:

Darstellung. 1,2 g Guanidincarbonat, in 10 ml Wasser gelöst und mit 1,2 ml Eisessig versetzt, wurden nach Abschluss der CO₂-Entwicklung mit 1 g p-Chinon in 15 ml Wasser auf 40° erwärmt, wobei die dunkelgefärbte Mischung allmählich eine feste, körnige Substanz ausschied. Nach 60 Min. wurde durch Schütteln der Lösung mit Chloroform unverändertes Chinon entfernt, worauf das schwarz-violette Produkt abfiltriert und mit Wasser und Chloroform gewaschen wurde. Ausbete 400 mg, Schmp. 300°.

Die Subst. 502 ist ein wenig löslich in Wasser und in Methanol, schwer löslich in Äthylacetat und Chloroform, ziemlich leicht löslich in Alkali, woraus sie durch Mineralsäuren gefällt wird.

Bei der Reduktion mit Zn und Essigsäure geht die Subst. 502 in Lösung und kann dann mit Äthylacetat extrahiert werden. Aus der mit wasserfreiem Natriumsulfat getrockneten Äthylacetat-Schicht wird nach dem Eindunsten im Vacuum ein gelbes Harz erhalten, das noch nicht zur Kristallisation gebracht werden konnte.

Keimungsversuche an Kresse (*Lepidium sativum*) mit Guanidyl-Chinon (502)

Die Samen in 3 Versuchsreihen 1–3 Stunden in Wasser, dann in Lösungen von 10–50 mg/100 ml bei 20°, pH 6,5 gequollen. Dann mit den gleichen Lösungen zwischen Filtrierpapier in Schalen zum Keimen gebracht.

Nach 6 Tagen mittlere Längen in mm:

Konzentration der Lösungen	Mit 502 behandelt		Wasserkontrolle	
	Wurzeln	Stengel	Wurzeln	Stengel
0,05 %	1–2, braun	5–10, gekrümmt	25–35	20–30
0,025 %	5–8	10–16		
0,01 %	15–20	20–25		
0,005 %	18–25	22–27		

Die Konzentrationen 0,05 und 0,025 % rufen in den ersten Keimungstagen eine starke Verzögerung der Keimung hervor.

¹ S. A. WAKSMAN, Streptomycin, Nature and Practical Applications. Baltimore 1949. — The Literature on Streptomycin 1944–1952. Rutgers University Press 1952.

**Zusammenfassung der Vorversuche (BETH VON EULER)
an Yoshida-Ascites-Sarkom-Ratten mit Guanidyl-p-Chinon (502)**

Die Versuchsdaten werden ausführlich in einer Mitteilung an anderer Stelle angegeben.

Methodik A. Intraperitoneale Injektion der Sbst. 502 in physiol. Kochsalzlös., pH 7,3–7,7, unmittelbar nach der Injektion von 0,1 ml des frischen Ascites (2 mg) und an den darauffolgenden Tagen je 2 mg.

Gewicht der Ratten zu Beginn des Versuchs: 103–105 g. Lebensdauer im Parallelversuch: 4,5 Tage.

4 Versuche. 9 g injiziert. Lebensdauer 7 Tage. Sehr wenig Ascites. Bei der Decapitierung nach 7 Tagen geringe Bildung von festem Tumor. Tumorale Bildungen an Diaphragma und Leber. Zusammenwachsungen am Magen und Darm.

Im ganzen deutliche Verzögerung der Tumor-Entwicklung; Rückgang des Tumors konnte nicht beobachtet werden.

Methode B. Intraperitoneale Injektion der *Mischung* von Ascites und Lösung der Sbst. 502, nach Inkubationszeit von 22 Stunden bei 0°. Parallelversuche mit Mischung der gleichen Ascites-Menge mit physiologischer Kochsalzlösung und genau gleicher Inkubationszeit. Die angewandten Dosen 502 wurden zwischen 0,5 und 2 mg variiert.

In 5 Versuchen ergab sich hier eine deutliche *Erhöhung der Lebensdauer* von 5 auf 11 Tage bzw. eine Hemmung der Ascites-Tumor-Entwicklung.

Im Anschluss an die Versuche mit Yoshida-Sarkom-Ratten wurden Versuche an Jensen-Sarkom-Ratten angestellt, die wir Herrn Prof. Dr. H. DRUCKREY verdanken. Die Injektion an diesen Ratten erfolgte subcutan neben dem Jensen-Sarkom. Rückgang der Jensen-Sarkome (ca 5 g) nach Injektion von 8 mg (4×2 mg) Guanidyl-Chinon nicht sicher festgestellt.

Herrn Ingenieur H. WÄHLSTAM danken wir für eifrige Mitarbeit bei der Darstellung und spektrometrischen Untersuchung der Präparate.

Stockholm, Universität, Institut für organisch-chemische Forschung und Vitamin-Institut.

Tryckt den 5 september 1956

Uppsala 1956. Almqvist & Wiksells Boktryckeri AB

Synthesis of thiamine diphosphate from added thiamine monophosphate by baker's yeast

By KARL-HEINZ KIESSLING

The ability of yeast to transform added thiamine into TDP¹ has been studied by several authors (1, 2, 3, 4). The present investigation deals with the problem if TMP can be used in connection with baker's yeast for synthesis of TDP without TMP first being hydrolyzed to thiamine, that is, if a stepwise phosphorylation can occur. It was planned to carry through the synthesis with a system deviating as little as possible from the intact yeast. TMP was added to the yeast, and the transformation of TMP to TDP was followed by aid of radioactive phosphate.

Different treatments of the yeast before synthesis were tried to make the cells permeable to TMP. Also the phosphatases which seem to occur in abundance on the surface of the yeast cells, had to be inhibited.

Experimental and results

Inhibition of the yeast phosphatases

It has been shown, among others, by Westenbrink, Van Dorp, Gruber and Veldman (5) that yeast has very strong phosphatases which gradually and in a very short time hydrolyse added TDP to thiamine and inorganic phosphate. In the present investigation different ways were tried of inhibiting the hydrolysis of TMP before penetration into the cells. No pH could be found at which the phosphatases were inactive, while the thiaminokinase (enzyme synthesizing TDP) still worked. At pH 2.6 or 7.1 the synthesis was slow compared with the optimal pH, but the phosphatases were still active.

Different chemical inhibitors have been mentioned in the literature. Those tested here were sodium fluoride, L-tartrate and molybdate. At lower pH none of these were especially efficient, but at pH 6 molybdate at a concentration of 10^{-3} M inhibited the hydrolysis to such an extent that about 70 % of the added TMP still remained after two hours' incubation. The high concentration of molybdate required may be explained by the fact that very dense yeast suspensions (15 g to 45 ml suspension) were used. TMP was added in an amount of 1.5 mg and the hydrolysis was followed by means of paper chromatography.

¹ Abbreviations: TTP thiamine triphosphate, TDP thiamine diphosphate, TMP thiamine monophosphate, ATP adenosine triphosphate.

The ability of TMP to penetrate into the yeast cell

TMP together with molybdate was added to a suspension of fresh baker's yeast in a succinate buffer pH 6, and incubated at 27° for 60 minutes. The yeast was then centrifuged down, washed twice with succinate buffer, and analysed for TMP by means of paper chromatography. The chromatographic method of Siliprandi and Siliprandi (6) was used. No appreciable amounts of TMP could be detected inside the cells. On the other hand the amount of TDP was higher there than at the beginning of the incubation. TDP could either have been synthesized directly from TMP penetrating into the cells or from thiamine derived from TMP by dephosphorylation.

To make sure whether thiamine phosphates can pass through the cell membrane yeast was enriched in thiamine phosphates by incubation with an excess of thiamine for 16 hours according to Westenbrink *et al.* (4), then washed, and incubated again for 60 minutes in the same kind of buffer, but now without thiamine. The cells were then centrifuged down, and the clear supernatant examined for thiamine phosphates. Only thiamine was found. Thus either all thiamine phosphates were bound inside the cells or the cell walls were impermeable to thiamine phosphates.

The same experiment was made with yeast treated in different ways to make the surface permeable. Plasmolysis with solid NaCl (20%) for five minutes, drying, treating with acetone, and freezing-thawing three times were methods tried. The ability to synthesize TDP was only slightly influenced except when using acetone-washed yeast, when it was absolutely inhibited. With dried or plasmolyzed yeast only thiamine and traces of TDP could be detected outside the cells. With yeast pretreated by freezing-thawing both thiamine, TMP, TDP, and TTP could be observed. In the following experiments yeast treated by plasmolysis with solid NaCl or by freezing-thawing was used. Thus the synthesis of TDP from TMP in yeast permeable to TMP could be compared with that in yeast which did not give off any thiamine phosphates to the surrounding medium. In this connection it has to be postulated that the passage of TMP through the cell membrane in one direction implies also the opposite possibility.

Synthesis of TDP from TMP

Yeast either plasmolyzed with solid NaCl or frozen and thawed three times was incubated with TMP and inorganic radioactive phosphate. Phosphatase activity was inhibited by molybdate. As molybdate very likely would bind the phosphate in the medium, P³² was added 60 minutes before molybdate and TMP, and was therefore already distributed inside the cells when molybdate was added. Then TDP synthesis was allowed to go on for at least 60 minutes, TDP was isolated by adsorption on Fuller's earth, eluted, precipitated, and at last separated by two successive different paper chromatographic methods as described by Kiessling (7). The TDP obtained in this way was partly hydrolyzed in 1 M HCl for 20 minutes, partly wet ashed. Hereby the specific radioactivity of α P and β P of TDP could be determined. The same incubations were made with thiamine instead of TMP, and with thiamine and TMP together. The results are shown in Table 1.

Table 1. The ratio of radioactivity in α P and β P of TDP synthesized for thiamine, thiamine monophosphate and thiamine + thiamine monophosphate.

Addition	Yeast plasmolyzed with solid NaCl 20 % α P ³² / β P ³²	Yeast frozen and thawed three times α P ³² / β P ³²
T	1.04 (3)	1.02 $\pm$ 0.05 (8)
TMP	0.93 (4)	0.59 $\pm$ 0.03 (7)
T + TMP . . .	1.07 (2)	0.60 $\pm$ 0.04 (7)

P³² of TDP was measured in a *M* 6 liquid counter tube, β P hydrolyzed by boiling the TDP sample in *N* HCl for 20 minutes, α P split off by wet ashing, and phosphorus determined according to Berenblum and Chain (8). P³² was then determined as counts/10 minutes/ μ g P. The figures given are mean values, the numbers of experiments being stated in brackets.

Discussion

When incubating yeast either plasmolyzed or frozen and thawed with thiamine, the radioactivity of α P and β P of TDP synthesized during 60 minutes is about the same. This is seen from Table 1 where the ratio α P³²/ β P³² is about 1 in the two cases. The same takes place on incubating plasmolyzed yeast with TMP or T + TMP, indicating that no synthesis of TDP from TMP occurs. As no thiamine phosphates can pass out of the cells (see above) it is very likely that TMP cannot pass into the cells. This might account for this result. Thiamine on the other hand passes easily through the membrane (1, 2, 9). When only TMP is added the synthesis of TDP very likely depends on part of TMP being hydrolyzed to thiamine by phosphatases on the cell surface.

Adding TMP to yeast which has been exposed to freezing-thawing results in TDP with a lower radioactivity in α P than in β P. The ratio α P³²/ β P³² is therefore lower than 1 (0.59). Thus it is obvious that TDP can be synthesized from TMP by yeast, without previous hydrolysis to thiamine. This is contrary to the opinion of Weil-Malherbe (10), according to which TMP is first hydrolyzed to thiamine which is then phosphorylated to TDP by taking a pyrophosphate group from ATP. The present author's results, however, agree with those of Steyn-Parvé (11) working with a partly purified thiaminokinase which could synthesize TDP from TMP, but at a lower rate than from thiamine. The enzyme was isolated from baker's yeast, and contained no phosphatases. Van Thoai, Roche and Sfez (12) isolated a thiaminokinase from intestinal dog mucosa which gave TDP on addition of thiamine as well as of TMP.

From Table 1 it is seen that the addition of thiamine together with TMP does not alter the ratio α P³²/ β P³² compared with the system with TMP alone. The TDP synthesis from thiamine does not seem to interfere with that from TMP. From the present results it cannot be decided whether the synthesis of TDP from thiamine passes over TMP or is a direct pyrophosphorylation as suggested by Weil Malherbe for yeast (10) and by Leuthardt and Nielsen for animal tissues (13).

Summary

In order to make possible the penetration of thiamine monophosphate into the cell interior of baker's yeast, the latter was exposed to freezing-thawing and the phosphatase acting upon thiamine phosphates inhibited by molybdate. Yeast treated

in this way is able, to a certain degree, to synthesize thiamine diphosphate from thiamine monophosphate without first splitting it into thiamine.

ACKNOWLEDGEMENTS

I am indebted to Prof. P. E. Lindahl for the interest he has shown in my work and to Mrs. Margot Aunver for technical assistance. This work was made possible by a grant from the Swedish Natural Science Research Council.

Institute of Zoophysiology, Uppsala, Sweden.

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Tryckt den 12 september 1956

Uppsala 1956. Almqvist & Wiksells Boktryckeri AB

Configurational studies in the α -phenyl carboxylic acid series

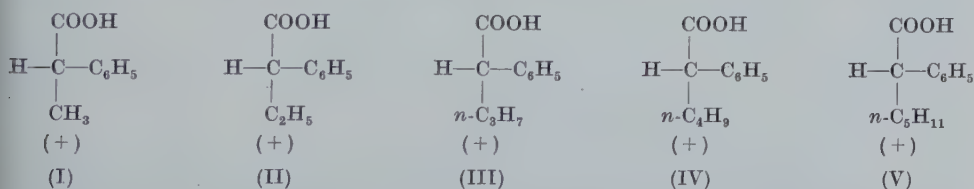
Hydratropic and α -phenylbutyric acids

By KURT PETTERSSON

With 16 figures in the text

The configuration of hydratropic acid (I) has been subjected to investigation by many authors. By several rearrangement reactions (+)-hydratropic acid has been converted to and sterically related to (-)- α -phenylethylamine. Oxidation of the phenyl group in the latter gives L-(+)-alanine. Since the consecutive reactions denote that the carboxyl group in alanine corresponds to the phenyl group in the hydratropic acid and the amino group in alanine corresponds to the carboxyl group in the hydratropic acid, L-(+)-alanine and (+)-hydratropic acid have opposite configurations, i.e. (+)-hydratropic acid belongs to the D-glyceraldehyde system. The same result was obtained by Mislow and Heffler, who made a thermal analysis of the amides of hydratropic and α -chlorphenylacetic acid. Finally, Fredga (1) related (+)-hydratropic acid and D-(+)-allylphenylacetic acid by means of their auxin activity and optical activity data. He also reviewed the literature on the field.

Whereas the configuration of hydratropic acid has attracted considerable interest, little has been done, as far as the author knows, to determine the configuration of the homologue, α -phenylbutyric acid (II) (10). Since the configurations of α -phenylvaleric (III), α -phenylcaproic (IV) and α -phenyloenanthic (V) acids have been determined (2), it is possible to connect (I) and (II) to (III) and thereby test the results obtained by previous authors.



The racemic acids (I) and (II) have been resolved into optical antipodes by means of the easily accessible enantiomeric α -phenylethylamines. Since these bases have not been used earlier for these resolutions, the details are given in the experimental part. The rotations of the optically active acids correspond with the best values reported in the literature (1, 3).

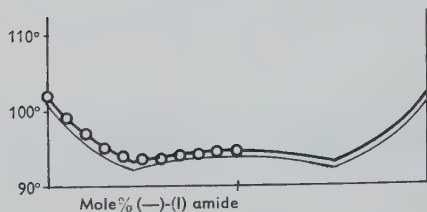


Fig. 1. (+)- and (-)-(I) amide.

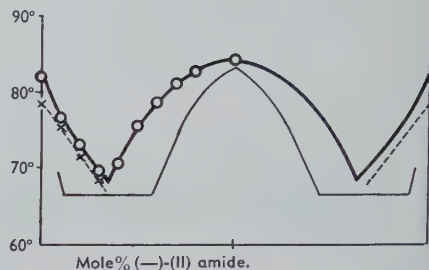


Fig. 2. (+)- and (-)-(II) amide.

The steric relation between the acids has been determined by means of three independent methods: the optical displacement rule, the quasi-racemate method applied to the amides, and the optical method, based upon comparing the optical activities in different solvents.

The well-known optical displacement rule, as formulated by Freudenberg (4), is an expression for the fact that chemically related substances with the same configuration undergo a shift of the optical activity in the same direction when converted to derivatives of the same kind. The acids (I), (II) and (III) fulfil the condition of chemical proximity, and thus the antipodes of these, for which the optical activities of amides, acids and anilides can be arranged in an increasing series, have the same configuration. From Table 1, where the values of $[M]_D^{25}$ in ethanol are given, it is apparent that this is the case for the antipodes with the same direction of rotation.

Table 1.

	Amide	Acid	Anilide
(-)-(I)	-69°	-119°	-271°
(-)-(II)	-92°	-129°	-253°
(-)-(III) (7)	-89°	-114°	-237°

Determination of configurations by means of the quasi-racemate method is founded on the fact that, in certain instances, one component in a racemate may be replaced by a chemically related compound with the same configuration. The resulting molecular compound has been called a quasi-racemate (5), since it in general is optically active. The existence of a quasi-racemate may be proved in several ways, for instance by thermal, X-ray diffraction, or infrared spectral methods. In this investigation the main emphasis is laid on the thermal method, in some cases completed with X-ray and infrared investigations.

The melting-point diagram of the optically active hydratropamides is shown in Fig. 1. At first sight one might feel tempted to suppose that optically inactive hydratropamide is a solid solution of the enantiomorphs. Further investigation of contact preparation shows, however, that it is true racemate, and X-ray and infrared investigations give further evidence for this conclusion.

Optically active hydratropamide crystallizes as needles from dilute ethanol and as glistening leaves from benzene-petroleum ether (6). However, the two preparations have the same melting point and identical X-ray powder photographs, and a

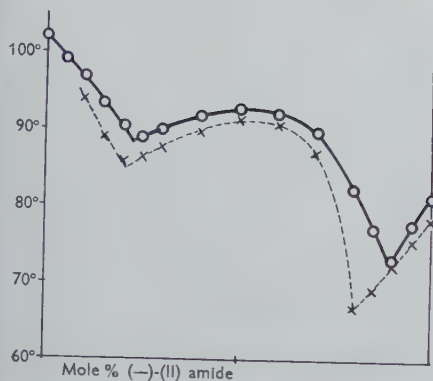


Fig. 3. (+)-(I) and (-)-(II) amide.

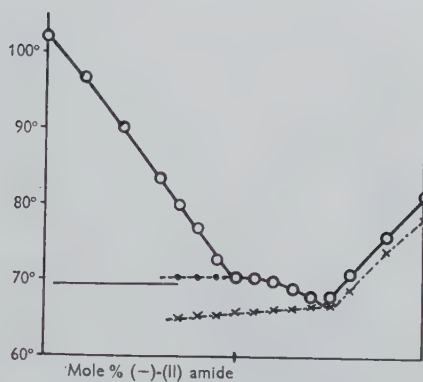


Fig. 4. (-)-(I) and (-)-(II) amide.

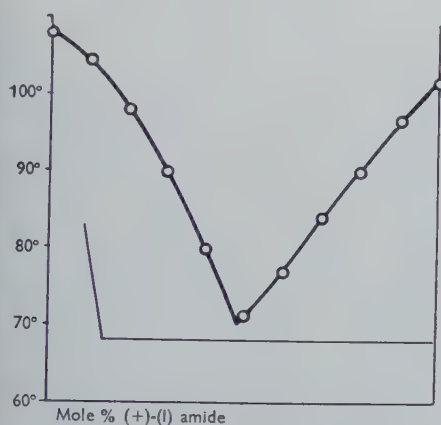


Fig. 5. (+)-(I) and (-)-(III) amide.

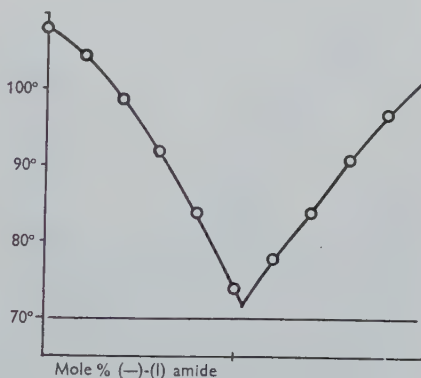


Fig. 6. (-)-(I) and (-)-(III) amide.

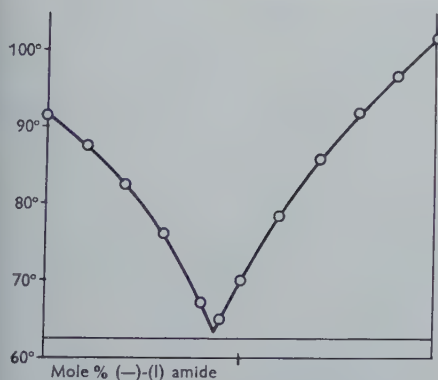


Fig. 7. (-)-(I) and (+)-(IV) amide.

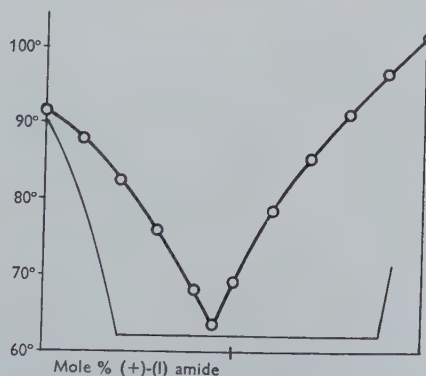


Fig. 8. (+)-(I) and (+)-(IV) amide.

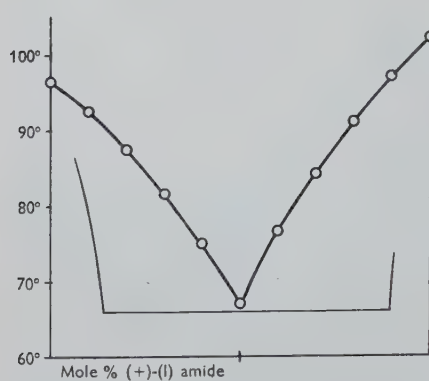


Fig. 9. (+)-(I) and (-)-(V) amide.

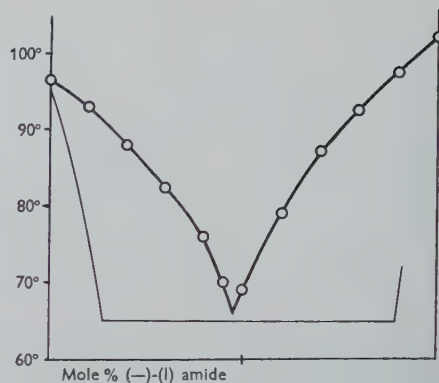


Fig. 10. (-)-(I) and (-)-(V) amide.

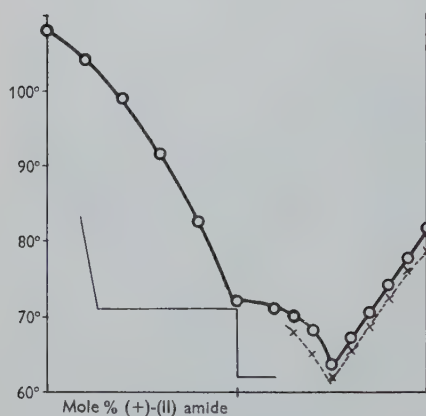


Fig. 11. (+)-(II) and (-)-(III) amide.

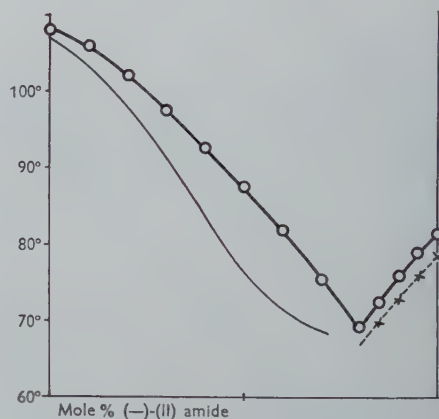


Fig. 12. (-)-(II) and (-)-(III) amide.

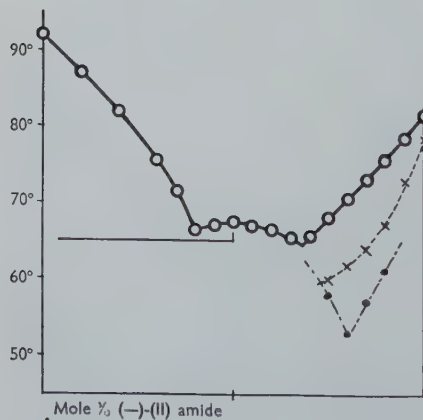


Fig. 13. (-)-(II) and (+)-(IV) amide.

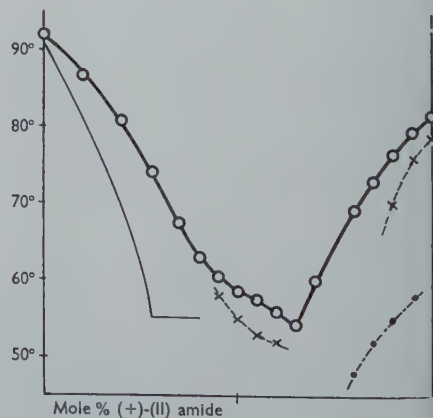


Fig. 14. (+)-(II) and (+)-(IV) amide.

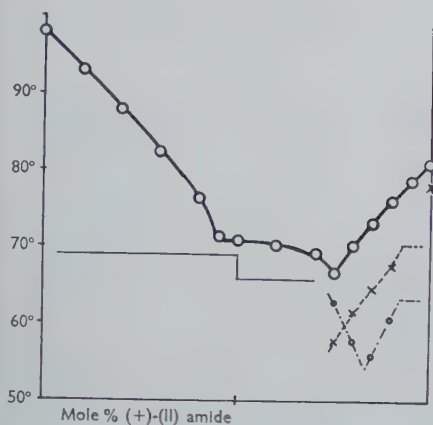


Fig. 15. (+)-(II) and (-)-(V) amide.

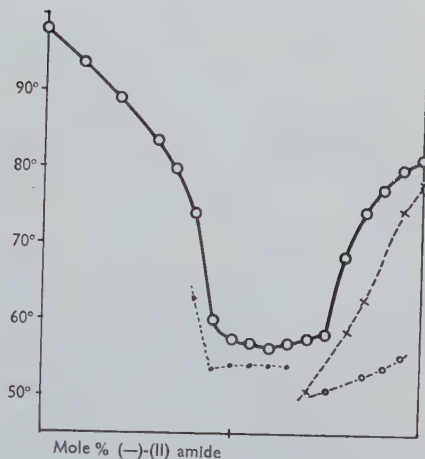


Fig. 16. (-)-(II) and (-)-(V) amide.

careful investigation in a hot-stage microscope gives no evidence for polymorphism, either for the racemic or for the enantiomeric hydratropamides.

The optically active α -phenylbutyramides exist in two modifications, but the racemic amide could be obtained in only one form (Fig. 2).

The success of the quasi-racemate method is dependent on several factors, among which the ability of racemate formation by and the steric differences between the enantiomeric compounds seem to be of special importance. From Fig. 1 it is evident that the enantiomorphs of hydratropamide, like those of α -phenylvaleramide (2), have a low tendency for racemate formation, whereas the enantiomeric α -phenylbutyramides (Fig. 2), like the corresponding amides of (IV) and (V), have a moderate tendency for such formation. When the steric differences and the racemate-formation tendency are taken into account, it is not surprising to find that the enantiomeric amides of (I) with the amides of (III), (IV) and (V) give only simple eutectic systems, supplying no information about the steric relation between the compounds (Figs. 5 through 10).

The two possible combinations of the optically active (I)- and (II)-amides require a more detailed inspection. The substances with opposite direction of rotation form a dimorphic molecular compound (Fig. 3), with the composition 1:1 and with an X-ray powder photograph different from those of the antipodes. Furthermore, the infrared spectrum contains three absorption bands in the N-H region (2.92, 3.05 and 3.16 microns), whereas the racemic and enantiomeric (I)- and (II)-amides give only two bands (3.0 and 3.18 microns). Even other differences exist, such as, for example, new bands at 12.75 and 13.40 microns.

The results are more difficult to interpret in the case of the amides with the same direction of rotation. The thermal and X-ray investigations indicate a molecular compound with the composition 1:1 (Fig. 4). The infrared spectrum seems, however, to be a sum of those of the components. This need not be a contradiction, since the infrared spectrum of optically inactive α -phenylbutyramide, clearly being a true racemate (Fig. 2), is almost identical with that of the optically active amide. It is probable, therefore, that the upper curve in Fig. 4 illustrates a molecular compound. It is then difficult to predict which of these two compounds in Figs. 3 and 4 constitutes

the quasi-racemate, and, strictly speaking, the method has failed to give information about the steric relation between the acids (I) and (II). However, it seems rather likely to the author that the more pronounced maximum in Fig. 3 represents the quasi-racemic compound.

A case where an enantiomeric substance gives molecular compounds with both antipodes of another is extremely rare, but has also been reported by Matell for the systems of α -(2,4,5-trichlorophenoxy)-propionic acid and α -(2-naphthoxy)-propionic acid (9).

The quasi-racemate method is more successful when applied to the amides of (II) and (III). Comparison of Figs. 11 and 12 leads to the conclusion that the molecular compound in Fig. 11 is a quasi-racemate. Therefore, the amides of (I) and (II) with the same direction of rotation have the same configuration, which is in agreement with the result of the optical displacement rule.

The dimorphism of the optically active (II)-amides give rise to complicated melting-point diagrams with the enantiomeric (IV)- and (V)-amides (Figs. 13–16). These amides are isomorphous (2), which may explain the fundamental resemblance between Figs. 13 and 15 and between Figs. 14 and 16. It is evident that Fig. 13 illustrates a quasi-racemate, which relates the configurations of (+)-(II) and (+)-(IV). In Fig. 15 is seen a molecular compound with the composition 1:1, which has also an X-ray powder photograph different from those of the components. The infrared spectrogram shows no significant differences from those of the components. In the middle of Fig. 16 is a region which is difficult to clear up with thermal methods. X-ray analysis indicates that the 1:1 composition is a mixture of the antipodes, which gives some support to the opinion that the molecular compound in Fig. 15 is a quasi-racemate. Thus, (+)-(II) is sterically connected to (+)-(III), (+)-(IV) and (+)-(V), which is in accordance with the steric results obtained earlier (2).

It is sometimes possible to obtain information of the configurational relation between two chemically related compounds by measuring the optical activities in some representative solvents. As is seen in Tables 2, 3 and 4, the optical activities of the acids, amides, and anilides change regularly when progressing down the series of solvents. The change is always in the same direction (increasing or decreasing) for the derivatives with the same sign of the rotation, and it may be concluded that these compounds have the same configuration.

The summarized facts in this paper evidently lead to the conclusion that the dextrorotatory hydratropic and α -phenylbutyric acids belong to the D-glyceraldehyde system, and the arrangement of the groups around the asymmetric carbon atom can according to the convention of Emil Fischer be represented by the formulae (I) and (II).

Table 2.

Solvent	[M] _D ²⁵ of acid		
	(-)-(I) (1)	(-)-(II)	(-)-(III) (7)
Acetone	-143.3°	-168°	-157°
Benzene	-139.8°	-157°	-136°
Acetic acid	-131.1°	-138°	-128°
Ether	—	-133°	-128°
Ethanol	-118.8°	-129°	-114°
Water (ion)	- 8.7°	- 11°	- 5°

Table 3.

Solvent	$[\alpha]_D^{25}$ of amide		
	(+)-(I)	(+)-(II)	(-)-(III) (7)
Acetic acid	+ 21°	+ 44°	- 49°
Ethanol	+ 69°	+ 92°	- 89°
Acetone	+ 70°	+ 92°	- 88°
Ether	+ 117°	+ 163°	- 163°
Benzene	+ 137°	+ 187°	- 172°

Table 4.

Solvent	$[\alpha]_D^{25}$ of anilide		
	(-)-(I)	(-)-(II)	(-)-(III) (7)
Acetone	- 216°	- 197°	- 184°
Acetic acid	- 216°	- 219°	- 212°
Ethanol	- 271°	- 253°	- 237°
Benzene	- 287°	- 327°	- 338°
Ether	- 344°	- 378°	- 363°

Experimental

Optical resolution of hydratropic acid

(-)- α -Phenylethylamine (-)-hydratropoate: 28 g (0.19 moles) of racemic hydratropic acid and 22.6 g of (-)- α -phenylethylamine were dissolved in a hot mixture of 400 ml of benzene and 100 ml of ethanol and allowed to crystallize. The precipitate was filtered off, washed with a small amount of cold benzene, dried and weighed. 0.4 g of the salt was set apart, the acid liberated with dilute sulfuric acid, extracted with ether and isolated by evaporation of the solvent. The acid was dissolved in ethanol and the optical activity measured in a 2 dm tube. The principal part of the salt was recrystallized from a mixture of benzene and ethanol 4:1 until the optical activity remained constant. The pure (-)-phenethylamine salt of (-)-hydratropic acid was obtained as colourless needles. The progress of the resolution is seen in Table 5.

(+)- α -Phenylethylamine salt of (+)-hydratropic acid: 17.5 g (0.12 moles) of hydratropic acid ($[\alpha]_D^{25} = +22^\circ$) and 14 g (0.12 moles) of (+)- α -phenethylamine were recrystallized from a 4:1 mixture of benzene and ethanol until the optical activity of the liberated acid remained constant. The results are collected in Table 5.

Table 5.

Crystallization number	ml of solvent	g of (-)-acid salt obtained	$[\alpha]_D^{25}$	ml of solvent	g of (+)-acid salt obtained	$[\alpha]_D^{25}$
1	500	16	- 65°	250	14	+ 75°
2	150	11.5	- 78°	87	9.6	+ 79°
3	87	8.7	- 78°	62	7.2	+ 80°
4	65	5.4	- 78°	42	6.1	+ 80°

K. PETTERSSON, *Hydratropic and α -phenylbutyric acids*

(-)-*Hydratropic acid*: The (-)-phenethylamine salt was decomposed with dilute sulfuric acid; the liberated acid was extracted with ether, and the solvent removed. The residue crystallized as transparent prisms, and was recrystallized from petroleum ether. M.p. 30–31°.

100.4 mg of the acid were dissolved in ethanol and made up to 10.00 ml.

$2\alpha_D^{25} = -1.577^\circ$, $[\alpha]_D^{25} = -78.4^\circ$ (lit. 79.1° (1)).

Amide: (-)-Hydratropic acid was refluxed with excess of thionyl chloride until the evolution of hydrochloric acid ceased (about 15 minutes) and the excess of thionyl chloride was removed *in vacuo*. The acid chloride was dissolved in benzene and the solution treated with concentrated ammonia. The benzene layer was washed with water and the solvent evaporated. The residue was recrystallized from a mixture of benzene and petroleum ether and from dilute ethanol. In the first case, the amide was obtained as glistening leaves; in the second, as colourless needles. In both cases, the melting point was 101.5–102°.

Anilide: The acid chloride, prepared as described for the amide, was dissolved in benzene and the solution treated with a solution of aniline and benzene. The anilinium chloride was dissolved in water, and the benzene layer was washed with 2*N* sulfuric acid and water. The solvent was removed and the anilide recrystallized from benzene-petroleum ether. Colourless needles, m.p. 99°–100°.

Optical activities in different solvents: Weighed amounts of the anilide were dissolved in the given solvent, made up to 10.00 ml, and the optical activity of the solution was measured in a 2 dm tube. The results are collected in Table 6.

Table 6.

Solvent	mg of anilide	$2\alpha_D^{25}$	$[\alpha]_D^{25}$	$[M]_D^{25}$
Ether	100.3	-3.065°	-152.7°	-344.1°
Benzene	93.0	-2.372°	-127.5°	-287.3°
Ethanol	112.4	-2.699°	-120.1°	-270.6°
Acetic acid	92.4	-1.773°	-95.9°	-216.2°
Acetone	111.1	-2.121°	-95.5°	-215.6°

(+)-*Hydratropic acid*: From the (+)-phenethylamine salt as described for its optical antipode. Transparent prisms, m.p. 30–31°.

100.4 mg of the acid was dissolved in 10.00 ml of ethanol.

$2\alpha_D^{25} = +1.582^\circ$, $[\alpha]_D^{25} = +78.9^\circ$ (lit. $+79.0^\circ$ (1)).

Amide: Glistening leaves, m.p. 101.5–102°. Optical activities in different solvents are collected in Table 7.

Table 7.

Solvent	mg of amide	$2\alpha_D^{25}$	$[\alpha]_D^{25}$	$[M]_D^{25}$
Benzene	92.8	$+1.700^\circ$	$+91.6^\circ$	$+136.7^\circ$
Ether	131.9	$+2.065^\circ$	$+78.3^\circ$	$+116.8^\circ$
Acetone	89.1	$+0.837^\circ$	$+47.0^\circ$	$+70.1^\circ$
Ethanol	97.8	$+0.909^\circ$	$+46.5^\circ$	$+69.3^\circ$
Acetic acid	129.7	$+0.369^\circ$	$+14.2^\circ$	$+21.2^\circ$

Optical resolution of α -phenylbutyric acid

(+)-Phenylethylamine (–)- α -phenylbutyrate: 31 g (0.19 moles) of racemic α -phenylbutyric acid and 23 g (0.19 moles) of (+)- α -phenethylamine were dissolved in a hot mixture of 300 ml of benzene and 75 ml of ethanol and allowed to crystallize. The salt was filtered off and recrystallized from a mixture of benzene and ethanol 4:1 in the same manner as described for hydratropic acid. The pure (+)-phenethylamine salt of (–)- α -phenylbutyric acid was obtained as colourless needles. The progress of the resolution is seen in Table 8.

(–)- α -Phenylethylamine (+)- α -phenylbutyrate: 17.0 g of α -phenylbutyric acid ($[\alpha]_D^{25} = +50^\circ$) and 12.5 g of (–)- α -phenethylamine were dissolved in a hot mixture of benzene and ethanol 4:1 and the resulting precipitate recrystallized until the optical activity of the liberated acid remained constant. The results are collected in Table 8.

Table 8.

Crystallization number	ml of solvent	g of (–)-acid salt obtained	$[\alpha]_D^{25}$	ml of solvent	g of (+)-acid salt obtained	$[\alpha]_D^{25}$
1	375	21	-60°	175	24	$+72^\circ$
2	125	19	-69°	143	19.5	$+77^\circ$
3	113	17	-77°	112	17.2	$+77^\circ$
4	100	15	-77°			

(–)- α -Phenylbutyric acid: The (–)-phenethylamine salt was decomposed with dilute sulfuric acid and the organic acid was extracted with ether. After evaporation of the solvent the acid remained as a colourless oil, which was distilled *in vacuo*. B.p. 102–104°/0.4 mm Hg.

156.8 mg of the acid required 19.22 ml of 0.0495N NaOH

$C_{10}H_{12}O_2$: Equiv. wt. calc. 164.2, found 164.8

Optical activity in homogenous state: $0.5\alpha_D^{23} = -47.9^\circ$, $[\alpha]_D^{23} = -95.8^\circ$ $[M]_D^{23} = -157.2^\circ$

Optical activities in different solvents are collected in Table 9.

Table 9.

Solvent	mg of acid	$2\alpha_D^{25}$	$[\alpha]_D^{25}$	$[M]_D^{25}$
Acetone	100.9	-2.058°	-102.0°	-167.5°
Benzene	100.6	-1.918°	-95.3°	-156.5°
Acetic acid	130.4	-2.191°	-84.1°	-138.1°
Ether	100.0	-1.617°	-80.9°	-132.8°
Ethanol	100.6	-1.580°	-78.5°	-129.0°
Water (ion)	100.2	-0.129°	-6.4°	-10.6°

Amide: Colourless needles, m.p. 80.5–81.5°. After premelting it melted at 78.5°.

Anilide: Colourless needles, m.p. 79.5–80.5. Optical activities in different solvents are collected in Table 10.

Table 10.

Solvent	mg of anilide	$2\alpha_D^{25}$	$[\alpha]_D^{25}$	$[M]_D^{25}$
Ether	88.3	- 2.789°	- 158.1°	- 378.3°
Benzene	93.9	- 2.569°	- 136.8°	- 327.2°
Ethanol	98.1	- 2.073°	- 105.7°	- 252.8°
Acetic acid	92.7	- 1.698°	- 91.6°	- 219.2°
Acetone	91.8	- 1.508°	- 82.1°	- 196.6°

(+)- α -Phenylbutyric acid: From the (-)- α -phenethylamine salt as described for the (-)-acid. Colourless oil b.p. 98–100°/0.3 mm Hg.

157.5 mg of the acid consumed 19.28 ml 0.0495N NaOH.

$C_{10}H_{12}O_2$: Equiv. wt. calc. 164.2, found 165.0. Optical activity in the homogenous state: $0.5\alpha_D^{23} = +47.7^\circ$, $[\alpha]_D^{23} = +95.4^\circ$, $[M]_D^{23} = +156.7^\circ$.

142.3 mg of the acid was dissolved in ethanol and made up to 10.00 ml.

$2\alpha_D^{25} = +2.236^\circ$, $[\alpha]_D^{25} = +78.6^\circ$, $[M]_D^{25} = +129.0^\circ$.

Amide: Colourless needles, m.p. 80.5–81.5°. After premelting 78.5°. Optical activity in different solvents are given in Table 11.

Table 11.

Solvent	mg of amide	$2\alpha_D^{25}$	$[\alpha]_D^{25}$	$[M]_D^{25}$
Benzene	113.5	+ 2.600°	+ 114.5°	+ 186.9°
Ether	89.3	+ 1.784°	+ 99.9°	+ 163.0°
Acetone	142.6	+ 1.613°	+ 56.6°	+ 92.3°
Ethanol	119.2	+ 1.348°	+ 56.6°	+ 92.3°
Acetic acid	87.5	+ 0.471°	+ 26.9°	+ 43.9°

Melting-point diagrams

The amides of the optically active acids (I) and (II) give with each other and with the optically active amides of (III), (IV), and (V) sixteen different two-component combinations. The results are collected in Figs. 1 through 16 and in Tables 12 through 27.

Melting-point preparations: Stock solutions of the amides in acetone were prepared, and the desired mixtures were obtained by mixing known amounts of the stock solutions. The solvent was removed and the residue carefully powdered and dried in a desiccator. The melting points were observed in a Kofler hot stage microscope. The lower melting points, as shown by the dotted curves in the figures were obtained after premelting and rapid cooling of the samples under a cover-glass. Where three curves are shown, there occurred two successive cycles of melting and crystallizing and a final melting at the original melting point. In the tables, having several columns, these lower melting points are given in the two first columns.

X-ray powder photographs were taken in a focusing camera of Guinier type with CuK radiation (45 kV, 22 mA), using an aluminium single crystal with double curvature as monochromator (8). Time of exposure 15 minutes.

Table 12. (+)- and (-)-(I) amide.

% (-)-amide	Melting point, °C
0	101.5-102
5	97.5- 98.5
10	96 - 97
15	94 - 95
20	93 - 94
25	92.5- 93.5
30	92.5- 93.5
35	93 - 94
40	93.5- 94
45	93.5- 94.5
50	94 - 94.5

Table 13. (+)- and (-)-(II) amide.

% (-)-amide	Melting point, °C	
0	78.5	81 -81.5
5	75.5	68.5-76.5
10	71.5	66.5-72.5
15	68	66.5-69.5
20		66.5-70.5
25		66.5-75.5
30		68 -78.5
35		74 -81
40		79 -82.5
50		83 -84

Table 14. (+)-(I) and (-)-(II) amide.

Mole % (-)-(II) amide	Melting point, °C	
0		101.5-102
5		99
10	94	96.5
15	89	93.5
20	86	90.5
25	86.5	89
30	88	90.5
40	90	92
50	91.5	93
60	91	92.5
70	87.5	90
80	87	83
85	69.5	77.5
90	72.5	73.5
95	76	77
100	78.5	81.5

Table 15. (-)-(I) and (-)-(II) amide.

Mole % (+)-(II) amide	Melting point, °C		
0			101.5-102
10			70 - 96.5
20			69.5- 90
30			69 - 83.5
35	65	70.5	80
40	65.5	70.5	77
45	65.5	70.5	73
50	66		70.5
55	66		70.5
60	66.5		70
65	66.5		69
70	67		68
75	67		68
80	69		71
90	74		76
100	78.5		81.5

Table 16. (+)-(I) and (-)-(III) amide.

Mole % (+)-(I) amide	Melting point, °C
0	106 -108
10	78 -104.5
20	68 - 98
30	68 - 90
40	68 - 80
50	68 - 71
60	68 - 77
70	68 - 85
80	68 - 90
90	68 - 97
100	101.5-102

Table 17. (-)-(I) and (-)-(III) amide.

Mole % (-)-(I) amide	Melting point, °C
0	106 -108
10	70 -104.5
20	69 - 98.5
30	70 - 92
40	70 - 84
50	69 - 74
60	69 - 78
70	69 - 84
80	70 - 91
90	70 - 97
100	101.5-102

Table 18. (+)-(I) and (+)-(IV) amide.

Mole % (+)-(I) amide	Melting point, °C
0	90 - 91.5
10	80 - 88
20	62 - 82.5
30	62 - 76
40	62 - 68
45	62 - 63.5
50	62 - 69
60	61.5- 78.5
70	62 - 85.5
80	62.5- 91.5
90	65 - 97
100	101.5-102

Table 20. (+)-(I) and (-)-(V) amide.

Mole % (+)-(I) amide	Melting point, °C
0	95.5- 96.5
10	80 - 92.5
20	66 - 87.5
30	66 - 81.5
40	66 - 75
50	65 - 67
60	66 - 77
70	66 - 84
80	66 - 91
90	70 - 97
100	101.5-102

Table 22. (+)-(II) and (-)-(III) amide.

Mole % (+)-(II) amide	Melting point, °C	
0		106-108
10		80-104
20		71- 99
30		71- 91.5
40		71- 82.5
50		71- 72
60		62- 71
65	68	70
70	65.5	67
75	62	63.5
80	65	68
85	68.5	70.5
90	72.5	74.5
95	76	77.5
100	78.5	81.5

Table 19. (-)-(I) and (+)-(IV) amide.

Mole % (-)-(I) amide	Melting point, °C
0	90 - 91.5
10	62 - 87.5
20	62 - 82.5
30	62 - 76.5
40	62 - 67
45	62 - 65
50	61 - 70
60	62 - 78.5
70	62.5- 86
80	62 - 92
90	62.5- 97
100	101.5-102

Table 21. (-)-(I) and (-)-(V) amide.

Mole % (-)-(I) amide	Melting point, °C
0	95.5- 96.5
10	75 - 93
20	65 - 88
30	65 - 82.5
40	65 - 76
45	65 - 70
50	65 - 69
60	65 - 79
70	66 - 87
80	65 - 92.5
90	70 - 97.5
100	101.5-102

Table 23. (-)-(II) and (-)-(III) amide.

Mole % (-)-(II) amide	Melting point, °C	
0		106 -108
10		102.5-106
20		97 -102.5
30		90 - 98
40		84 - 92.4
50		76 - 87.5
60		71 - 82
70		68.5- 75.5
80		68 - 69.5
85	70	72.5
90	73	76
95	76	79
100	78.5	81.5

Table 24. (-)-(II) and (+)-(IV) amide.

Mole % (-)-(II) amide	Melting point, °C		
0			90-91.5
10			65-87
20			65-82
30			65-75.5
35			65-71.5
40			65-66.5
45			65-67
50			65-67.5
55			60-67
60			60-66.5
65			60-65.5
70	(63)		65.5
75	58	60	68
80	55	62	70.5
85	57	64	73
90	60	67	75.5
95	(63)	73	78.5
100		78.5	81.5

Table 25. (+)-(II) and (+)-(IV) amide.

Mole % (-)-(II) amide	Melting point, °C		
0			90-91.5
10			80-86.5
20			69-81
28			55-74
35			55-67.5
40			55-63
45		58.5	60.5
50		55	58
55		53	57.5
60		52	56
65			54
70			60
80	48		69
85	52		73
90	55	70	77
95	58	76	79.5
100		78.5	81.5

Table 26. (+)-(II) and (-)-(V) amide.

Mole % (+)-(II) amide	Melting point, °C		
0			95-96.5
10			70-93
20			69-88
30			69-82.5
40			69-76.5
50			69-71
60			67.5-71
70			67-69.5
75	63	58	67
80	58	62	70.5
85	56	65	73.5
90	61	68	76.5
95	(61)	(68)	79
100		78.5	81.5

Table 27. (-)-(II) and (-)-(V) amide.

Mole % (-)-(II) amide	Melting point, °C		
0			95-96.5
10			85-93.5
20			77-89
30			68-83.5
35			80
40		63	74
45		53.5	60
50		54	57.5
55		54	57
60		54	56.5
65		54	57
70		51	57.5
75	51		58.5
80		59.5	68.5
85	53	65	74.5
90	54		77.5
95	56	75	80
100		78.5	81.5

Summary

Hydratropic and α -phenylbutyric acids have been resolved into optical antipodes by means of the enantiomeric α -phenylethylamines.

The *dextro*-rotatory hydratropic and α -phenylbutyric acids have been related to D-glyceraldehyde *via* α -phenylvaleric acid. The methods used are:

(a) The optical displacement rule, applied to the amides, acids, and anilides.

(b) The quasi-racemate method, applied to the amides. The sixteen possible melting-point diagrams of the enantiomeric amides of hydratropic and α -phenylbutyric acids with each other and with the enantiomorphs of α -phenylvaleric, α -phenylcaproic, and α -phenyloenanthic amides were investigated by thermal, X-ray, and infrared methods.

(c) The optical activities of hydratropic and α -phenylbutyric acid and their amides and anilides in different solvents were compared with the corresponding values of α -phenylvaleric acid, amide, and anilide.

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